Supporting Information

Electronic Effects of Aluminum Complexes in the Copolymerization of Propylene Oxide with Tricyclic Anhydrides: Access to Well-Defined, Functionalizable Aliphatic Polyesters

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I. General Considerations

All manipulations of air and water sensitive compounds were carried out under nitrogen in an MBraun Labmaster glovebox or by using standard Schlenk line technique. ^{1}H NMR spectra were recorded on Varian INOVA 400 (^{1}H, 400 MHz), INOVA 500 (^{1}H, 500 MHz), or INOVA 600 (^{1}H, 600 MHz) spectrometers. Spectra were referenced to the residual chloroform (7.26 ppm) or DMSO-d_5 (2.50 ppm) signals. ^{13}C NMR spectra were recorded on a Varian INOVA 500 (^{13}C, 126 MHz) spectrometer and referenced to the residual chloroform (77.23 ppm) or DMSO-d_6 (39.50 ppm) signals. ^{19}F NMR spectra were recorded on a Varian INOVA 400 (^{19}F, 376 MHz) spectrometer, and ^{31}P NMR spectra were also recorded on a Varian INOVA 400 (^{31}P, 162 MHz) spectrometer. HRMS analyses were performed on a Thermo Scientific Exactive Orbitrap MS system equipped with an Ion Sense DART ion source.

MALDI-TOF-MS analyses were performed on a Waters Micro MX system with a 10 Hz N_2 UV laser and based on a previously reported procedure.[1] Crude polymer samples were dissolved in THF at 1 mg·mL^{-1}. Potassium trifluoroacetate was used as the cationization agent and dissolved in THF at 5 mg·mL^{-1}. The matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was dissolved in THF at 40 mg·mL^{-1}. Solutions for analysis were prepared by mixing polymer, cationization agent, and matrix solutions in a volume ratio of 80:10:40, respectively. The sample was left to air dry after spotting on a stainless steel MALDI target plate. All spectra were recorded in linear mode and mass-locked to the residual signal of $[PPN]^+$ (538 *m*/*z*). The resulting spectra were analyzed using the MassLynx 4.0 software package.

Flash column chromatography was performed using silica gel (particle size 40–64 μm, 230–400 mesh). Gel permeation chromatography (GPC) analyses were carried out using an Agilent Technologies PL-GPC 50 Integrated GPC equipped with a refractive index detector and a Polymer Laboratories PL-AS RT GPC autosampler, an Agilent 1260 Infinity GPC System equipped with a refractive index detector and an Agilent 1260 Infinity autosampler, or a Waters 1515 Isocratic HPLC pump equipped with a Waters 2414 Refractive Index Detector and a Waters 2707 autosampler. The Agilent GPC systems were equipped with two PL gel Mini-MIX C columns (5 micron, 4.6 mm ID), which were eluted with THF at 30 °C at 0.3 mL/min and calibrated using monodisperse polystyrene standards. The Waters GPC system was equipped with three PSS SDV columns (5 micron, 5 mm ID), which were eluted with THF at 40 °C at 1.0 mL/min and calibrated using monodisperse polystyrene standards. The GPC systems gave comparable molecular weight and dispersity data.

II. Materials

Solvents used for cyclic anhydride and ligand syntheses, including methanol (Macron), absolute ethanol (Koptec), methylene chloride (Fisher), hexanes (Macron), ethyl acetate (Fisher), chloroform (Fisher), and diethyl ether (J. T. Baker), were used as received. Toluene (Fisher) and hexanes (Fisher) used in salicylaldehyde and complex syntheses were dried and degassed by passing them through two columns packed with neutral alumina and copper(II) oxide. Racemic propylene oxide (PO) was purchased from Aldrich, stirred over CaH_2 for three days, vacuum transferred to a dry Strauss flask and then degassed by three freeze-pump-thaw cycles. Bis(triphenylphosphine)iminium chloride [(PPN)Cl, 97%, Aldrich] was recrystallized by layering a saturated methylene chloride solution with diethyl ether. The resulting crystals were ground to a fine powder and then dried at 60 °C under vacuum prior to use. All other chemicals and reagents were purchased from commercial sources (Aldrich, Combi-Blocks, Strem, Acros, TCI America, and Alfa Aesar) and used without further purification.

The ligand *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene [(salph-^{t}**Bu**)H_2][2] and the complex **2a**[3] were prepared according to literature procedures. The following cyclic anhydrides were also synthesized according to literature procedures: *rac*-*cis*-*endo*-1-isopropyl-4-methyl-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (**1a**),[4] *cis*-*endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (**1b**),[4] *cis*-*endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**1c**),[5] *cis*-*endo*-bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (**1d**),[6] and *rac*-*cis*-*endo*-2-methyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**1e**).[5] All cyclic anhydrides were dried at 22 °C under vacuum for at least one day and then stored in a glovebox.

III. General Synthetic Procedures

Procedure A: Formylation of phenols to corresponding salicylaldehyde derivatives. An oven-dried flask equipped with a side arm and a magnetic stir bar was charged with the appropriate phenol (1.0 equiv.), 2,6-lutidine (1.5 equiv.), and dry, degassed toluene. After cooling the mixture to 0 °C, tin(IV) chloride was added dropwise via syringe. The resulting yellow slurry was warmed to 22 °C and stirred for at least 20 minutes before adding paraformaldehyde (5.0 equiv.). The headspace was partially evacuated, and the reaction was sealed and then stirred at 90 °C for 22 h. After cooling to 22 °C, 2 M HCl was added and the biphasic mixture stirred for 1 hour. The layers were separated, and the aqueous phase was extracted with diethyl ether (3x). The combined organic layers were washed with brine and saturated sodium bicarbonate solution,

dried with anhydrous $MgSO_4$, filtered, and then concentrated by rotary evaporation. The residue was purified via flash column chromatography and then recrystallization if necessary.

Procedure B: Formation of salph ligands via imine condensation. The appropriate salicylaldehyde SA-**X** (2.0 equiv.) was dissolved with either methanol or ethanol. After adding 1,2-diaminobenzene (1.0 equiv.), the reaction mixture was refluxed for the indicated time. The reaction mixture was then cooled to 22 °C, and the resulting precipitate was isolated by filtration. The solids were washed with small amounts of cold methanol or ethanol to give the corresponding salph ligands after drying under vacuum at 60 °C overnight.

Procedure C: Metallation of salph ligands with Et_2AlCl. In a glovebox, (salph-**X**)H_2 (1.0 equiv.) was dissolved in dry, degassed toluene in a dry Schlenk flask. A solution of Et_2AlCl (1.0 M in toluene, 1.1 equiv.) was added dropwise with stirring, resulting in the precipitation of yellow solids from the reaction mixture. After stirring at 22 °C for 5 minutes in the glovebox, the flask was sealed and removed from the glovebox. The mixture was then heated at 90 °C for 16 h. After cooling to 22 °C, the resulting solids were filtered, washed with dry, degassed hexanes, and dried under vacuum overnight.

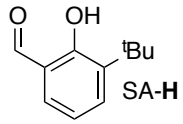
Procedure D: Copolymerization of propylene oxide with cyclic anhydrides. In a glovebox, the appropriate amount of metal complex and [PPN]Cl were placed in an oven-dried 4-mL vial equipped with a magnetic stir bar. The appropriate amount of cyclic anhydride was added, followed by PO. The vial was sealed with a Teflon-lined cap, removed from the glovebox, and placed in an aluminum heating block preheated to 60 °C. After the appropriate amount of time, an aliquot was taken for ^{1}H NMR spectroscopic analysis to determine conversion of the cyclic anhydride. The reaction mixture was then diluted with approximately 0.5 mL methylene chloride and precipitated into 10 mL of methanol with vigorous stirring, after which the methanol was decanted. Precipitation was repeated as necessary to remove excess monomer and catalyst. The polymer was dried under vacuum at 60 °C.

Procedure E: Monitoring of M_n, M_w/M_n, conversion of cyclic anhydride, and relative stereochemistry of polymer diester units as a function of time for the copolymerization of PO with cyclic anhydrides. In a glovebox, **1c** (1.47 g, 8.96 mmol), [PPN]Cl (46.3 mg, 80.6 μmol), and metal complex (89.6 μmol) were weighed into a 20-mL flame-dried vial equipped with a magnetic stir bar. PO (3.15 mL, 44.8 mmol) and dry, degassed THF (1.00 mL) were added, and the vial sealed with a Teflon cap. The reaction mixture was stirred at 22 °C for approximately

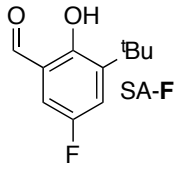
5 minutes until the mixture became homogeneous. The solution was then evenly divided into seven 0.75 mL portions in 4-mL flame-dried vials equipped with magnetic stir bars. After sealing the vials with Teflon lined caps, they were removed from the glovebox and stirred at 60 °C in a pre-heated aluminum heating block. For each polymerization, the vial was removed from the heating block at the specified time, and an aliquot was taken for ^{1}H NMR analysis to determine conversion of cyclic anhydride. The remaining reaction mixture was precipitated into approximately 10 mL of methanol and vigorously stirred. The methanol was decanted and the precipitated polymer was triturated with methanol to further remove catalyst and unreacted anhydride. The resulting polymer was then dried overnight under vacuum at 60 °C.

Procedure F: Diblock copolymer synthesis. For the initial block, 6.8 mg **2c** (13 μmol) and 6.6 mg [PPN]Cl (12 μmol) were placed in an oven-dried 4-mL vial equipped with a magnetic stir bar in a glovebox, followed by **1c** (52 mg, 0.32 mmol), PO (0.11 mL, 1.6 mmol), and 0.20 mL dry, degassed THF. The resulting homogenous mixture was transferred via pipet to a 2-mL Schlenk bomb and sealed with a Teflon Kontes valve. It was removed from the glovebox and placed in an aluminum heating block preheated to 60 °C for 3 h. The polymerization was returned to the glovebox and an aliquot was taken for ^{1}H NMR and GPC analyses. For the second block, a solution of **1d** (54 mg, 0.32 mmol), PO (0.11 mL, 1.6 mmol) and 0.20 mL dry, degassed THF were added directly to the reaction mixture via pipet. The Schlenk bomb was again sealed with a Teflon Kontes valve, removed from the glovebox, and returned to the aluminum heating block preheated to 60 °C for 6 hours. An aliquot was then taken for ^{1}H NMR and GPC analyses. The reaction mixture was precipitated into 10 mL of methanol with vigorous stirring, after which the methanol was decanted. Precipitation was repeated as necessary to remove catalyst. The polymer was dried under vacuum at 60 °C.

IV. Synthesis of Salicylaldehydes

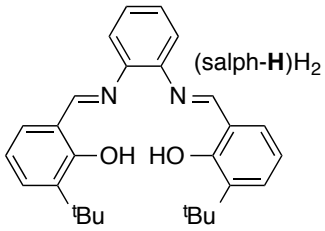


3-*tert*-Butylsalicylaldehyde (SA-H). Prepared according to the literature procedure.[7] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.79 (s, 1H), 9.88 (s, 1H), 7.52 (dd, 1H), 7.39 (dd, 1H), 6.95 (t, 1H), 1.42 (s, 9H).

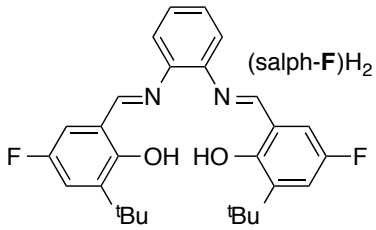


3-*tert*-Butyl-5-fluorosalicylaldehyde (SA-F). According to Procedure A, 4-fluoro-2-*tert*-butylphenol[8] (5.0 g, 30 mmol) was treated with tin(IV) chloride (1.7 mL, 15 mmol), 2,6-lutidine (5.2 mL, 45 mmol), and paraformaldehyde (4.5 g, 150 mmol) in toluene (100 mL). After purifying by column chromatography and recrystallizing from hexane, SA-**F** (2.4 g, 41%) was isolated as pale yellow needles. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.59 (s, 1H), 9.82 (s, 1H), 7.26–7.29 (m, 1H), 7.05–7.09 (m, 1H), 1.41 (s, 9H). **^{13}C NMR** (126 MHz, CDCl3): δ 196.26–196.35, 157.75–157.78, 156.38, 154.48, 141.23–141.28, 122.61, 122.42, 120.05-120.00, 115.75, 115.57, 35.32, 29.16. **HRMS** (DART-MS): *m/z* calculated for ($M-H^+$) 195.08268, found 195.08091.

V. Synthesis of Ligands

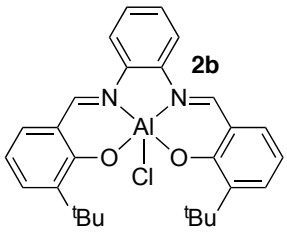


***N,N'*-Bis(3-*tert*-butylsalicylidene)-1,2-diaminobenzene [(salph-H)H_2].** According to Procedure B, SA-**H** (1.0 g, 5.8 mmol) and 1,2-diaminobenzene (0.30 g, 2.8 mmol) were refluxed in absolute ethanol (20 mL) to give (salph-**H**)H_2 (0.81 g, 67%) as an orange solid. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 13.73 (s, 2H), 8.66 (s, 2H), 7.38 (dd, 2H), 7.31–7.36 (m, 2H), 7.23–7.27 (m, 4H), 6.86 (t, 2H), 1.44 (s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 164.46, 160.98, 142.71, 138.02, 130.93, 130.69, 127.73, 119.87, 119.32, 118.36, 35.13, 29.56. **HRMS** (DART-MS): *m/z* calculated for $C_{28}H_{33}N_2O_2^+$ ($M+H^+$) 429.25365, found 429.25305.

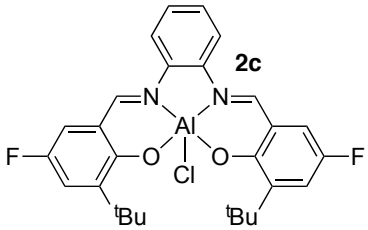


***N,N'*-Bis(3-*tert*-butyl-5-fluorosalicylidene)-1,2-diaminobenzene [(salph-F)H_2].** According to Procedure B, SA-**F** (2.0 g, 10 mmol) and 1,2-diaminobenzene (0.55 g, 5.1 mmol) were refluxed in methanol (25 mL) to give (salph-**F**)H_2 (1.9 g, 81%) as an orange microcrystalline solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.50 (s, 2H), 8.58 (s, 2H), 7.33–7.38 (m, 2H), 7.23–7.27 (m, 2H), 7.12 (dd, 2H), 6.93 (dd, 2H), 1.43 (s, 18 H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.53–163.56, 157.19, 156.15, 154.27, 142.34, 140.38–140.43, 128.12, 119.88, 118.63–118.69, 118.45, 114.97, 114.79, 35.36, 29.30. **HRMS** (DART-MS): *m/z* calculated for $C_{28}H_{31}F_2N_2O_2^+$ ($M+H^+$) 465.23481, found 465.23433.

VI. Synthesis of Aluminum Complexes



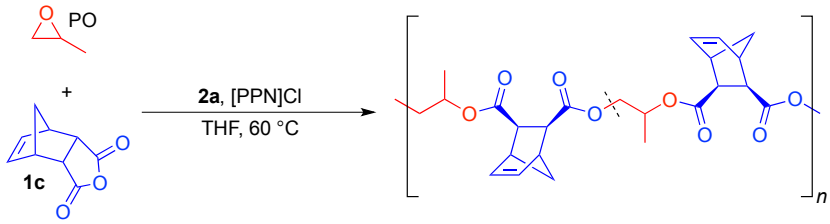
(salph-H)AlCl (2b). According to Procedure C, (salph-**H**)H_2 (0.30 g, 0.70 mmol) was treated with a 1.0 M solution of Et_2AlCl (0.75 mL, 0.75 mmol) in toluene (approx. 20 mL) to give **2b** (0.23 g, 69%) as a yellow powder. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.37 (s, 2H), 8.20–8.25 (m, 2H), 7.59–7.65 (m, 2H), 7.46–7.55 (m, 4H), 6.76–6.80 (m, 2H), 1.56 (s, 18H). **^{13}C NMR** (126 MHz, DMSO-d_6): δ 164.83, 161.63, 140.01, 137.35, 134.44, 133.32, 128.48, 119.71, 116.79, 115.99, 35.04, 29.62. **HRMS** (DART-MS): *m/z* calculated for $C_{28}H_{32}AlN_2O_3$ ($M-Cl^-+H_2O$) 471.22283, found 471.22177.



(salph-F)AlCl (2c). According to Procedure C, (salph-**F**)H_2 (0.23 g, 0.49 mmol) was treated with a 1.0 M solution of Et_2AlCl (0.54 mL, 0.54 mmol) in toluene (approx. 20 mL) to give **2c** (0.22 g, 85%) as a yellow microcrystalline solid. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.35 (s, 2H), 8.15–8.19 (m, 2H), 7.53–7.58 (m, 2H) 7.43 (dd, 2H), 7.29 (dd, 2H), 1.54 (s, 18H). **^{13}C NMR** (126 MHz, DMSO-d_6): δ 161.43, 160.94–161.24, 153.32, 151.48, 142.40, 137.19, 128.91, 121.50, 121.30, 118.66, 118.59, 117.10, 116.81–116.98, 35.30, 29.26. **^{19}F NMR** (376 MHz, DMSO-d_6): δ −128.03. **HRMS** (DART-MS): *m/z* calculated for $C_{28}H_{30}AlF_2N_2O_3$ ($M-Cl^-+H_2O$) 507.20399, found 507.20266.

VII. Supplementary Polymerization Data

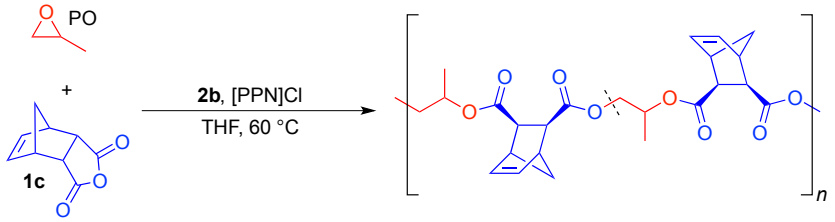
Table S1. Effect of conversion on polydispersity and diester stereochemistry in the copolymerization of PO and **1c** using **2a**.



entry[a]	time (h)	conv. (%)[b]	M_n (kDa)[c]	M_w/M_n[c]	% *cis*[d]
1	0.33	24	2.3	1.07	>99
2	0.67	65	6.8	1.13	>99
3	1.0	93	9.0	1.13	>99
4	1.5	>99	8.1	1.39	84
5	2.0	>99	8.6	1.48	72
6	3.0	>99	8.9	1.61	62
7	5.0	>99	6.4	1.97	49

[a] See Procedure E for experimental details, [PO]:[**1c**]:[**2a**]:[(PPN)Cl] = 500:100:1:0.9. [b] Conversion of cyclic anhydride, determined by ^{1}H NMR spectroscopy. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by ^{13}C NMR spectroscopy.

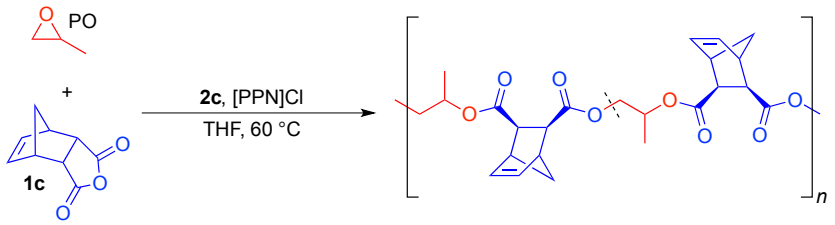
Table S2. Effect of conversion on polydispersity and diester stereochemistry in the copolymerization of PO and **1c** using **2b**.



entry[a]	time (h)	conv. (%)[b]	M_n (kDa)[c]	M_w/M_n[c]	% *cis*[d]
1	0.50	41	4.1	1.08	>99
2	0.75	62	5.2	1.13	>99
3	1.0	75	6.9	1.15	>99
4	1.5	>99	8.8	1.19	97
5	2.5	>99	7.2	1.33	87
6	3.5	>99	7.0	1.47	83
7	6.0	>99	6.3	1.72	76

[a] See Procedure E for experimental details, [PO]:[**1c**]:[**2b**]:[(PPN)Cl] = 500:100:1:0.9. [b] Conversion of cyclic anhydride, determined by ^{1}H NMR spectroscopy. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by ^{13}C NMR spectroscopy.

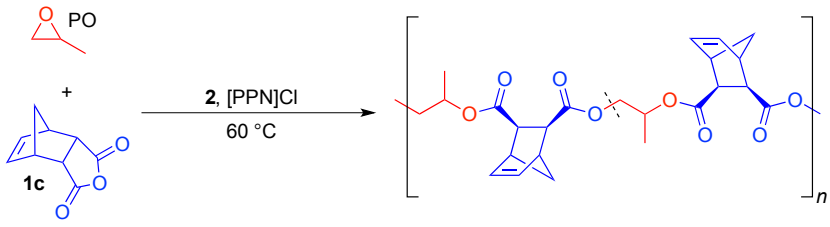
Table S3. Effect of conversion on polydispersity and diester stereochemistry in the copolymerization of PO and **1c** using **2c**.



entry[a]	time (h)	conv. (%)[b]	M_n (kDa)[c]	M_w/M_n[c]	% *cis*[d]
1	0.50	23	1.9	1.16	>99
2	0.75	37	3.7	1.07	>99
3	1.0	53	4.5	1.15	>99
4	1.5	65	5.9	1.16	>99
5	2.5	>99	9.8	1.16	>99
6	3.5	>99	9.8	1.16	>99
7	6.0	>99	9.7	1.17	>99

[a] See Procedure E for experimental details, [PO]:[**1c**]:[**2c**]:[(PPN)Cl] = 500:100:1:0.9. [b] Conversion of cyclic anhydride, determined by ^{1}H NMR spectroscopy. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by ^{13}C NMR spectroscopy.

Table S4. Effect of conversion on polydispersity and diester stereochemistry in the copolymerization of PO and **1c** using **2a**, **2b**, and **2c** in the absence of THF.



entry[a]	complex	time (h)	conv. (%)[b]	M_n (kDa)[c]	M_w/M_n[c]	% *cis*[d]
1	2a	0.67	84	8.1	1.15	>99
2	2a	5.0	>99	4.0	2.41	53
3	2b	0.75	68	6.9	1.13	>99
4	2b	6.0	>99	7.6	1.45	88
5	2c	0.75	44	4.2	1.15	>99
6	2c	6.0	>99	9.6	1.16	>99

[a] See Procedure D for experimental details, [PO]:[**1c**]:[**2**]:[(PPN)Cl] = 500:100:1:0.9. [b] Conversion of cyclic anhydride, determined by ^{1}H NMR spectroscopy. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by ^{13}C NMR spectroscopy.

VIII. Stability of [PPN]Cl under Copolymerization Conditions

According to Martinsen and Songstad,[9] $[PPN]^+$ undergoes slow degradation in warm, concentrated solutions of sodium hydroxide. Presumably, aluminum and $[PPN]^+$ alkoxides are present at the end of the copolymerization of epoxides with cyclic anhydrides when an excess of epoxide is used. To confirm that $[PPN]^+$ does not degrade under these copolymerization conditions, the residual $[PPN]^+$ at the end of a copolymerization was analyzed by ^{1}H and ^{31}P NMR spectroscopy. As described in Procedure D, 0.213 g **1c** (1.28 mmol) was copolymerized with 0.45 mL PO (6.4 mmol) using 15.6 mg **2a** (25.6 μmol) and 16.4 mg [PPN]Cl (28.2 μmol). After heating for 2 h at 60 °C, a large aliquot was taken and diluted with $CDCl_3$. The crude ^{1}H NMR spectrum revealed that full conversion of **1c** was achieved (Figure S1). The spectrum was consistent with an alternating copolymer with significant epimerization of diester stereochemistry. The residual aromatic signals of $[PPN]^+$ were consistent with the ^{1}H NMR spectrum of [PPN]Cl. Furthermore, the ^{31}P NMR spectrum revealed a single signal at 20.93 ppm (Figure S2), which is comparable to the ^{31}P NMR signal observed for [PPN]Cl in $CDCl_3$ (21.05 ppm).

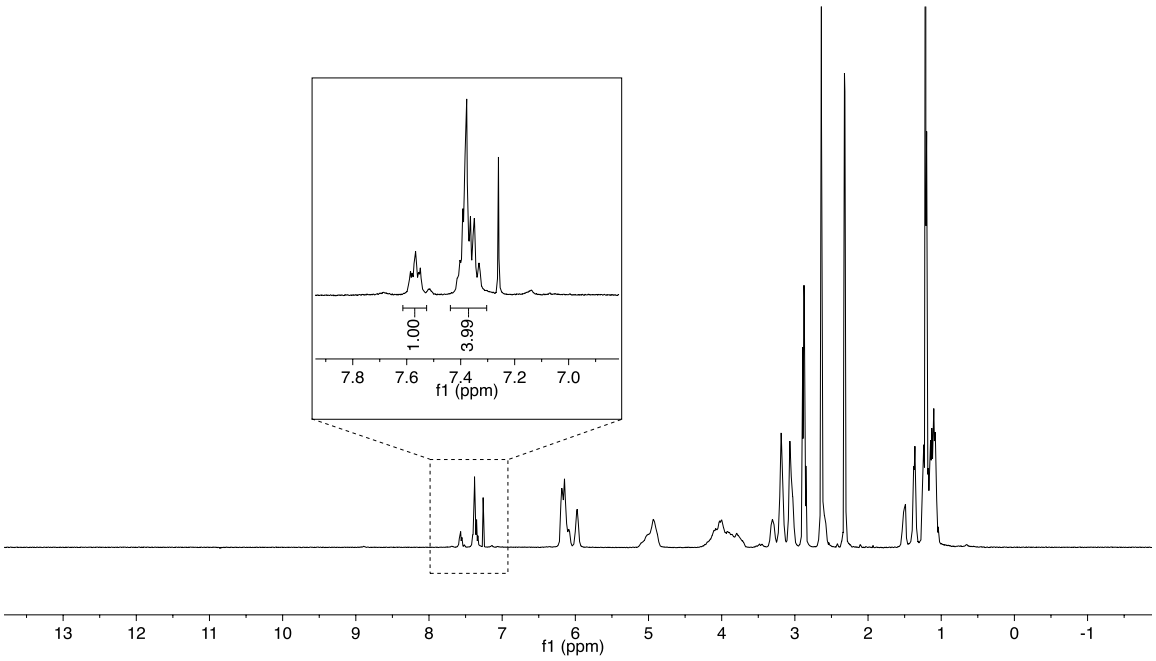


Figure S1. Crude ^{1}H NMR of the copolymerization of PO and **1c** using **2a** and [PPN]Cl. Inset is a magnified view of the aromatic protons of $[PPN]^{+}$.

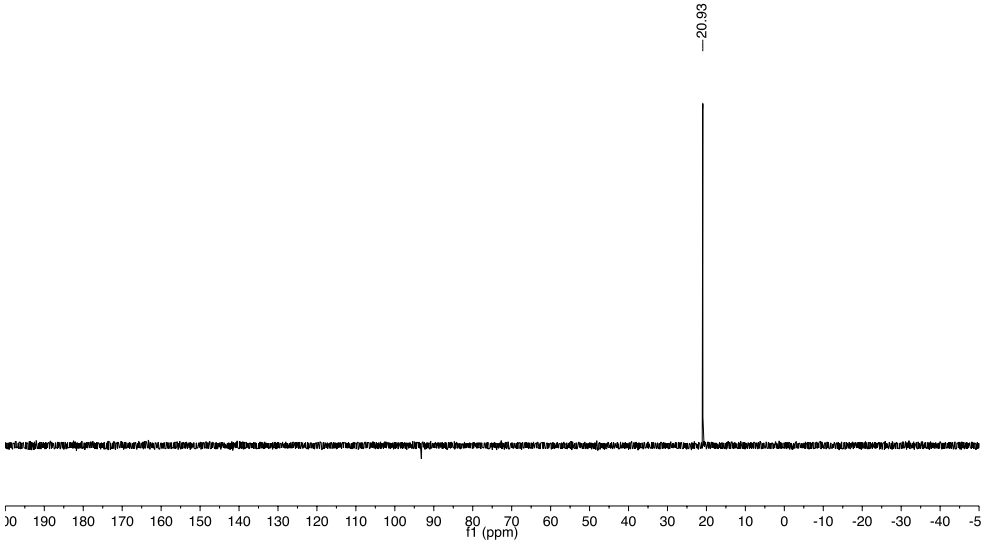


Figure S2. ^{31}P NMR spectrum of the crude polymerization mixture presented in Figure S1.

IX. Stereochemistry of Polymer Diester Units

The procedure for determining the stereochemistry of poly(**1c**-*alt*-PO) is based on previous literature precedent.[4] No epimerization is observed in the copolymerization of **1c** with PO when the reaction is quenched before reaching full conversion. The carbonyl region of the ^{13}C NMR

spectrum is diagnostic for diester stereochemistry for poly(**1c**-*alt*-PO). Using the poly(**1c**-*alt*-PO) described in Table S1, entry 3 as a representative example, only two carbonyl signals (171.50 and 172.04 ppm) are observed (Figure S3a, inset), which is expected for a highly regioregular copolymer. When the copolymerization is run to full conversion, the resulting polymer (such as the one described in Table 1, entry 3, t_{rxn} = 150 min) exhibits four new carbonyl signals at 173.90, 173.47, 172.75, and 172.28 ppm (Figure S3b, inset). These signals have approximately equal integration values. Given that **2a** is highly regioselective for ring-opening PO at its methylene carbon in copolymerizations with tricyclic anhydrides,[4] we propose that these new signals are attributable to the two possible *trans*-diester structures shown in Figure S4. The integration of these signals indicates that 58% of the diester units are *cis*. We confirmed these assignments and the % *cis* value by degrading the polymer with lithium aluminum hydride[4] and analyzing the resulting mixture of *cis*- and *trans*-diols (Figure S5).

The diester stereochemistry was determined by ^{13}C NMR spectroscopy in an analogous fashion for the other polymers reported in this work except for poly(**1e**-*alt*-PO). For poly(**1e**-*alt*-PO), we were unable to unambiguously determine the diester stereochemistry based on ^{13}C NMR spectroscopy alone. The diester stereochemistry for this polymer was confirmed by degrading the polymer with lithium aluminum hydride and analyzing the resulting mixture by ^{1}H NMR spectroscopy.

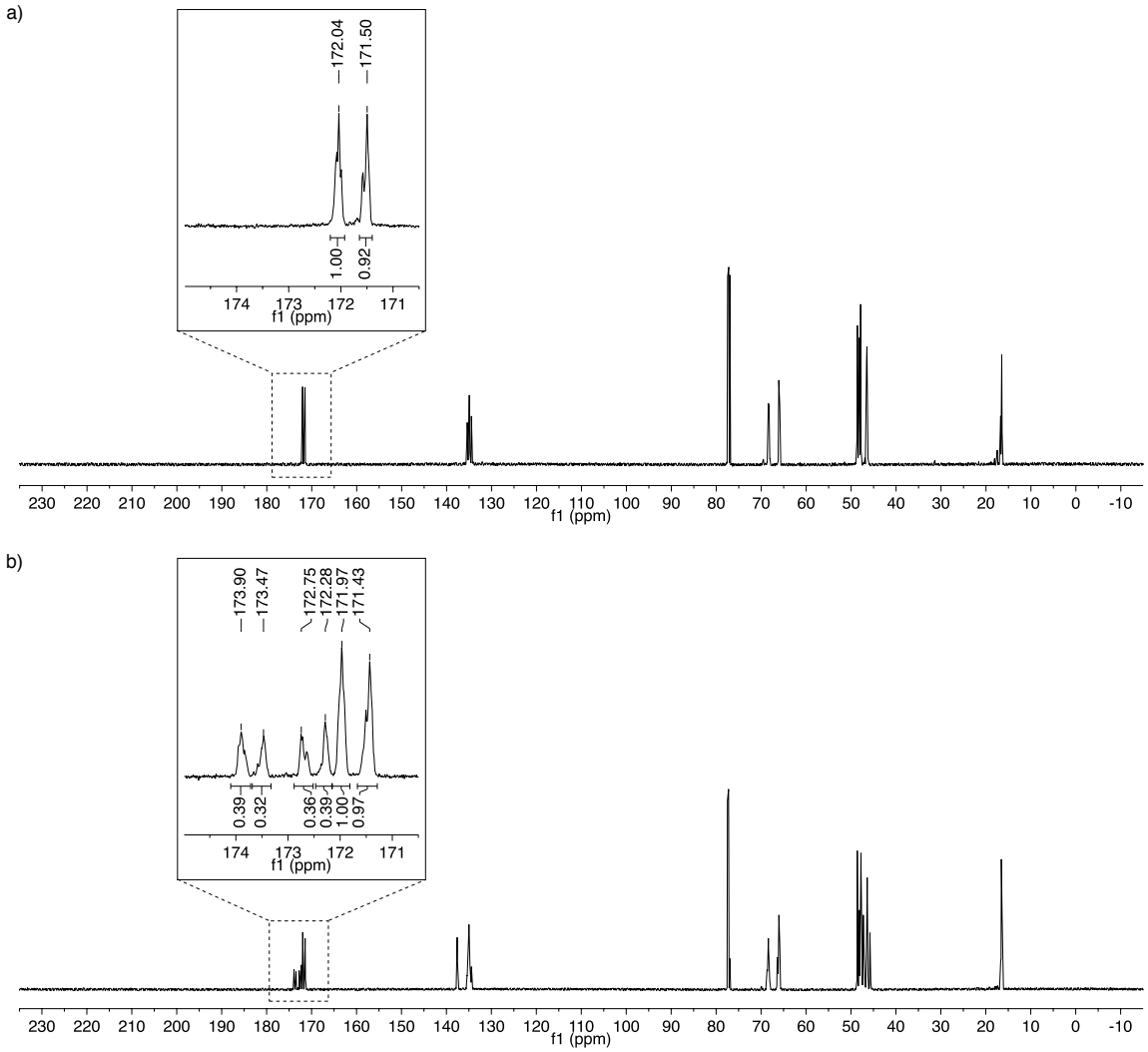


Figure S3. Comparison of the ^{13}C NMR spectra of poly(**1c**-*alt*-PO) synthesized using **2a** under the conditions of a) Table S1, entry 3 and b) Table 1, entry 3, t_{rxn} = 150 min. Insets are magnified views of the diagnostic carbonyl signals.

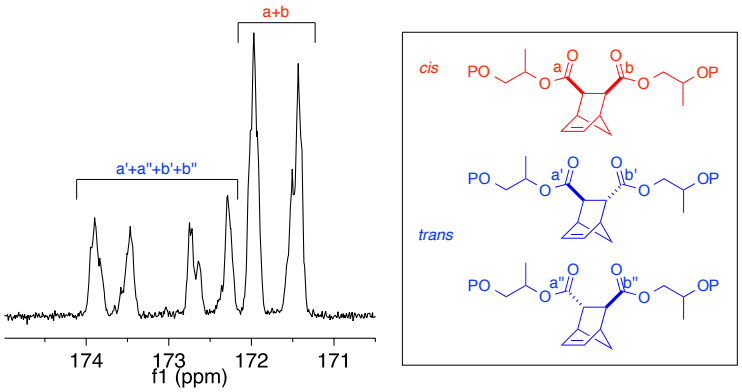


Figure S4. Assignment of carbonyl region of poly(**1c**-*alt*-PO) synthesized according to the conditions of Table 1, entry 3, t_{rxn} = 150 min.

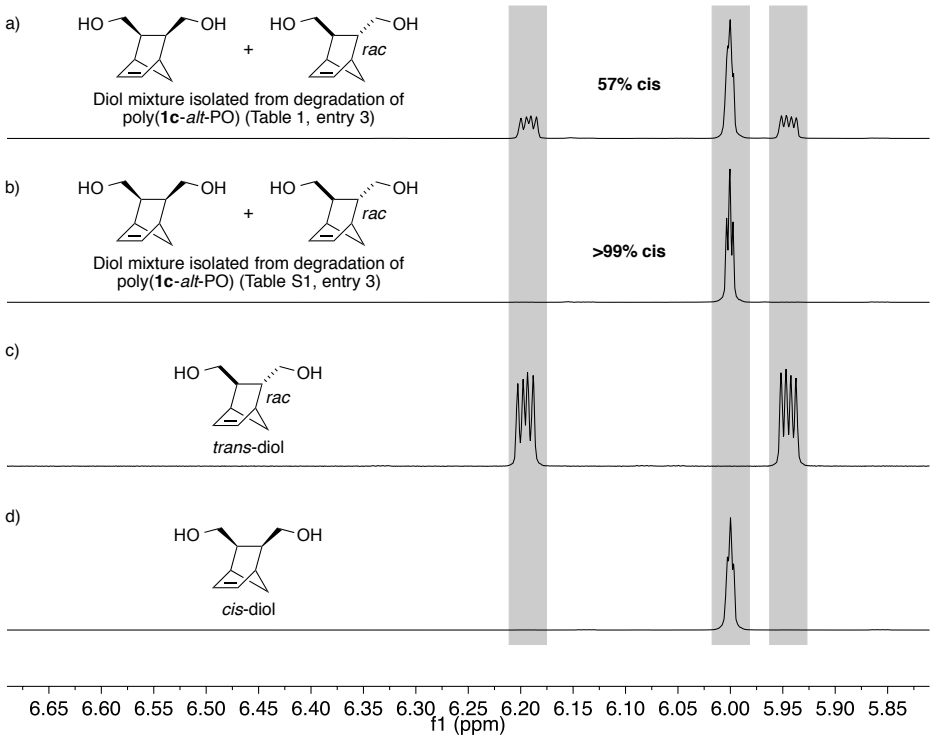


Figure S5. ^{1}H NMR spectra of the vinylic region of a) diol mixture isolated from the reductive degradation of poly(**1c**-*alt*-PO) (Table S1, entry 3); b) diol mixture isolated from the reductive degradation of poly(**1c**-*alt*-PO) (Table 1, entry 3, t_{rxn} = 150 min); c) *rac*-*trans*-bicyclo[2.2.1]hept-5-ene-2,3-dicarbinol;[10] and d) *rac*-*cis*-*endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarbinol.[10]

X. Diblock Copolymer Synthesis

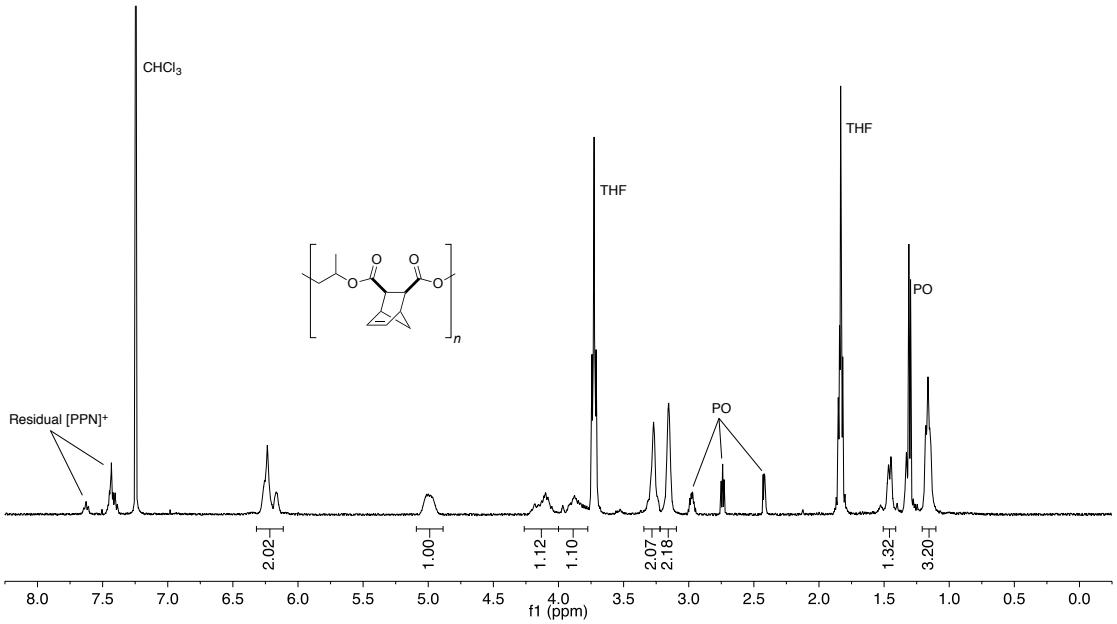


Figure S6. Crude ^{1}H NMR spectrum of poly(**1c**-*alt*-PO) produced en route to diblock copolymer according to Procedure F.

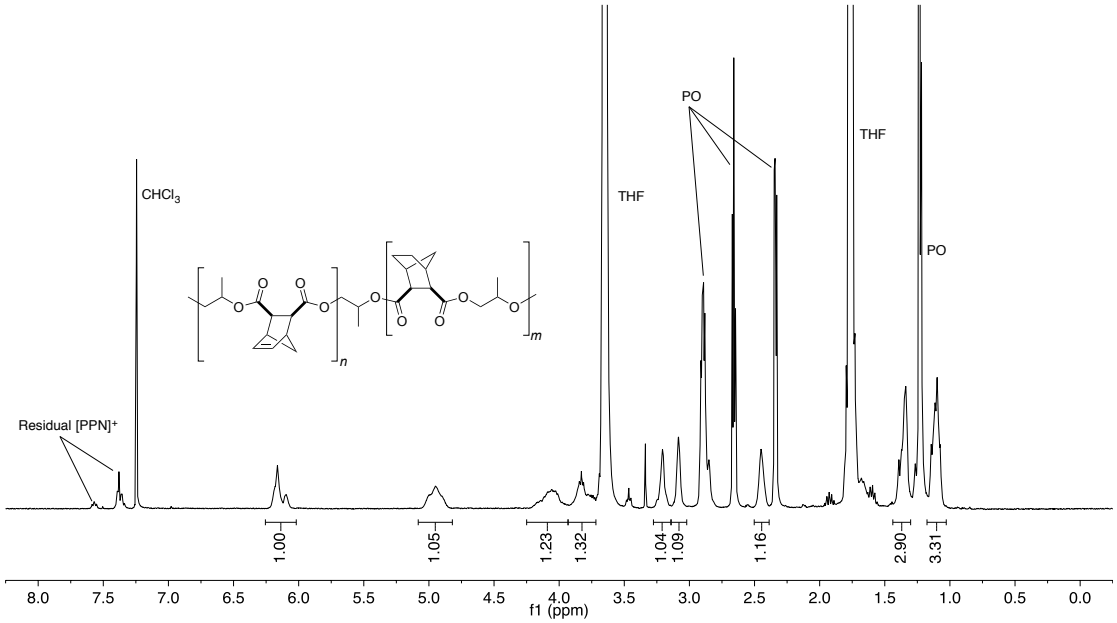
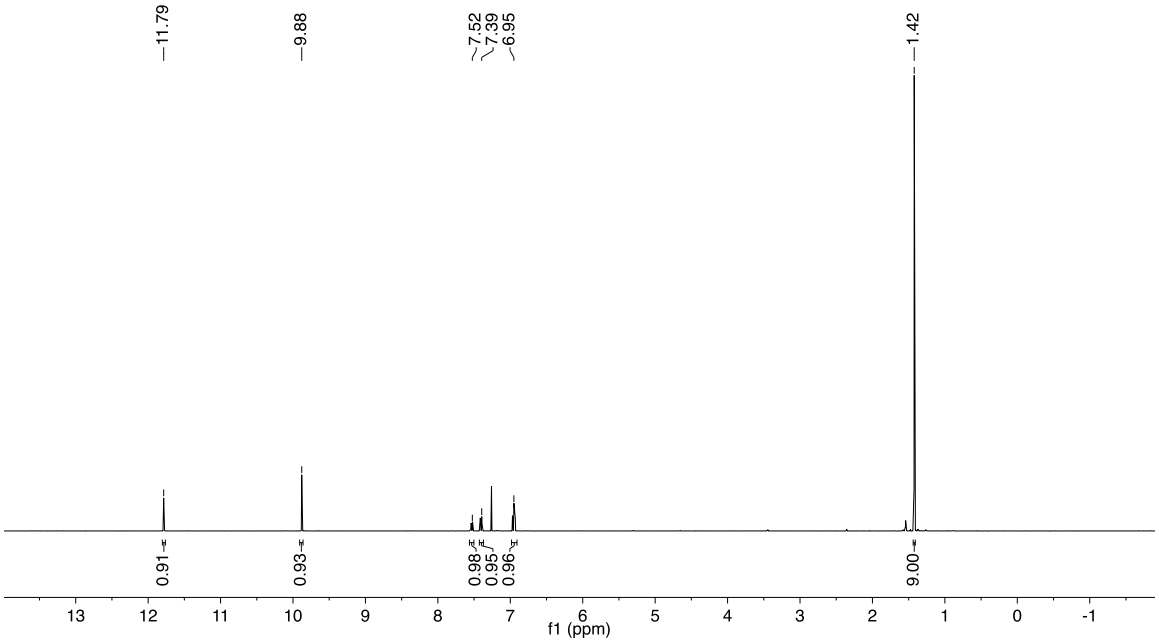


Figure S7. Crude ^{1}H NMR spectrum of poly[(**1c**-*alt*-PO)-*b*-(**1d**-*alt*-PO)] produced according to Procedure F.

XI. Copies of ^{1}H, ^{13}C, and ^{19}F NMR Spectra

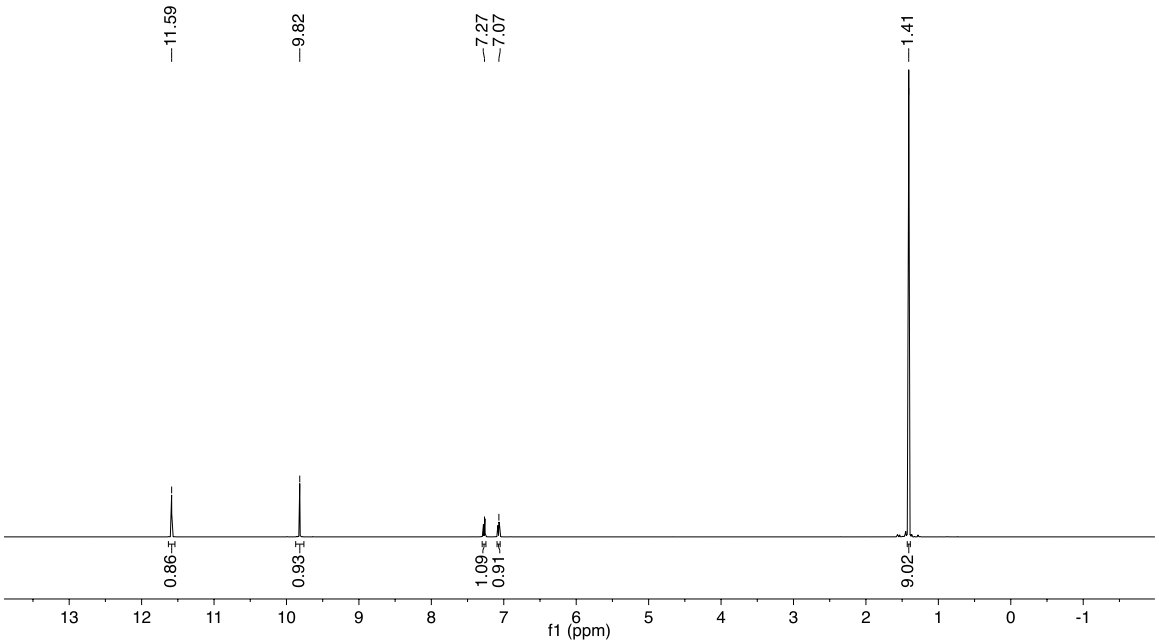
3-*tert*-Butylsalicylaldehyde (SA-H)

^{1}H NMR (400 MHz, $CDCl_3$)



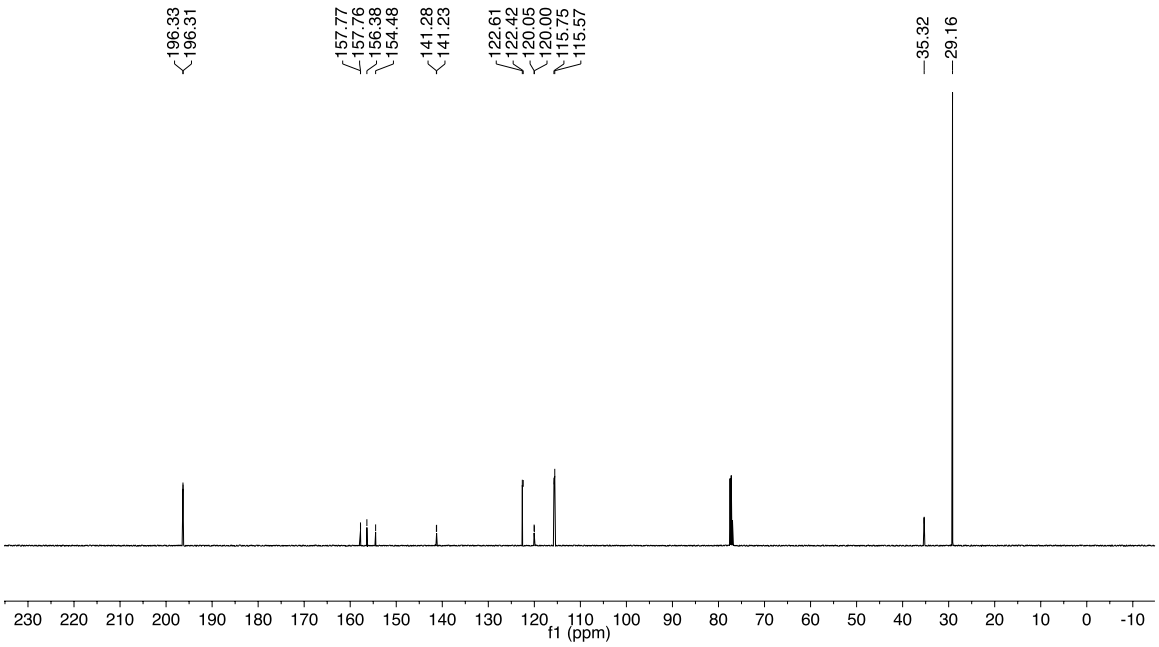
3-*tert*-Butyl-5-fluorosalicylaldehyde (SA-F)

^{1}H NMR (500 MHz, $CDCl_3$)



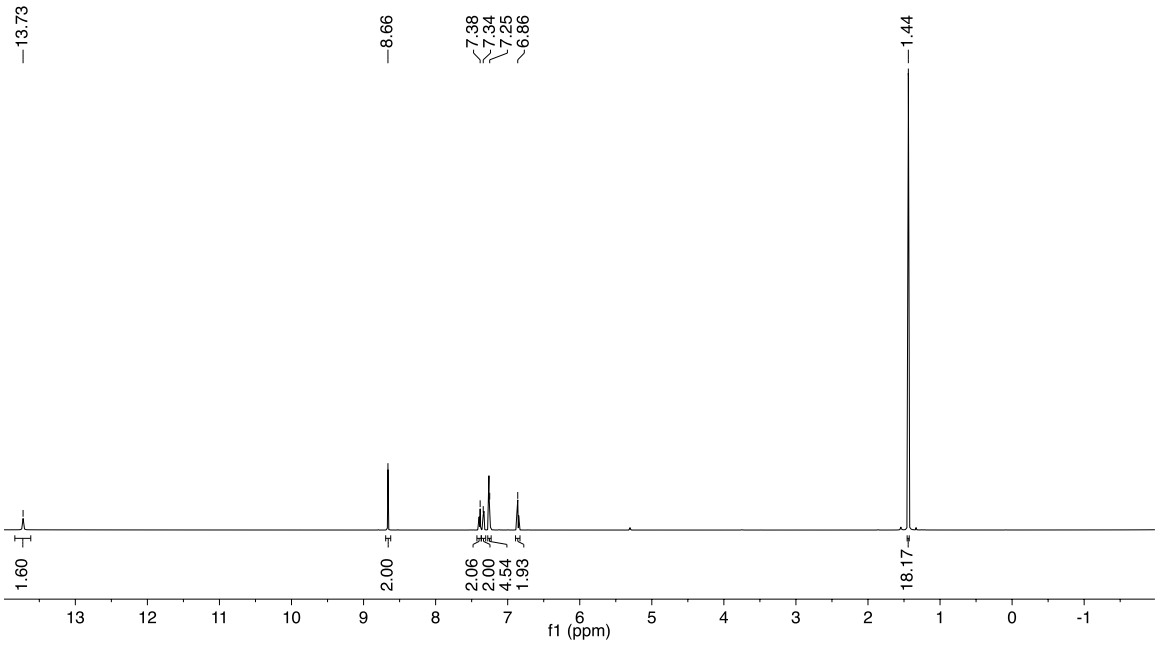
3-*tert*-Butyl-5-fluorosalicylaldehyde (SA-F)

^{13}C NMR (126 MHz, $CDCl_3$)



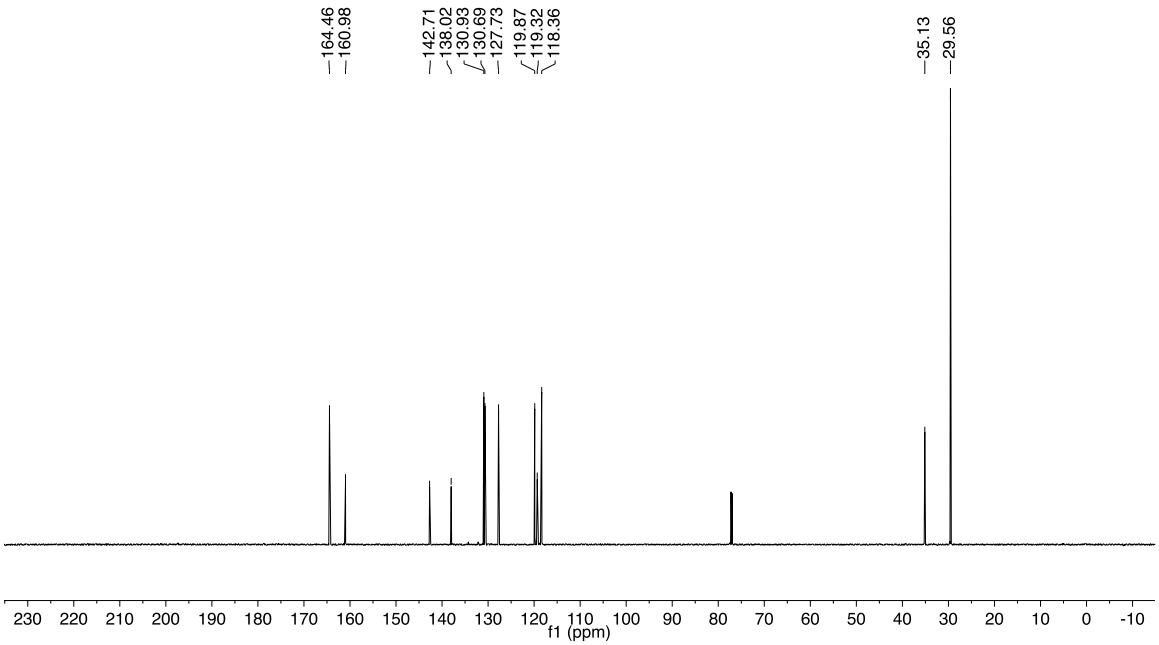
***N,N'*-Bis(3-*tert*-butylsalicylidene)-1,2-diaminobenzene [(salph-H)H_2]**

^{1}H NMR (600 MHz, $CDCl_3$)



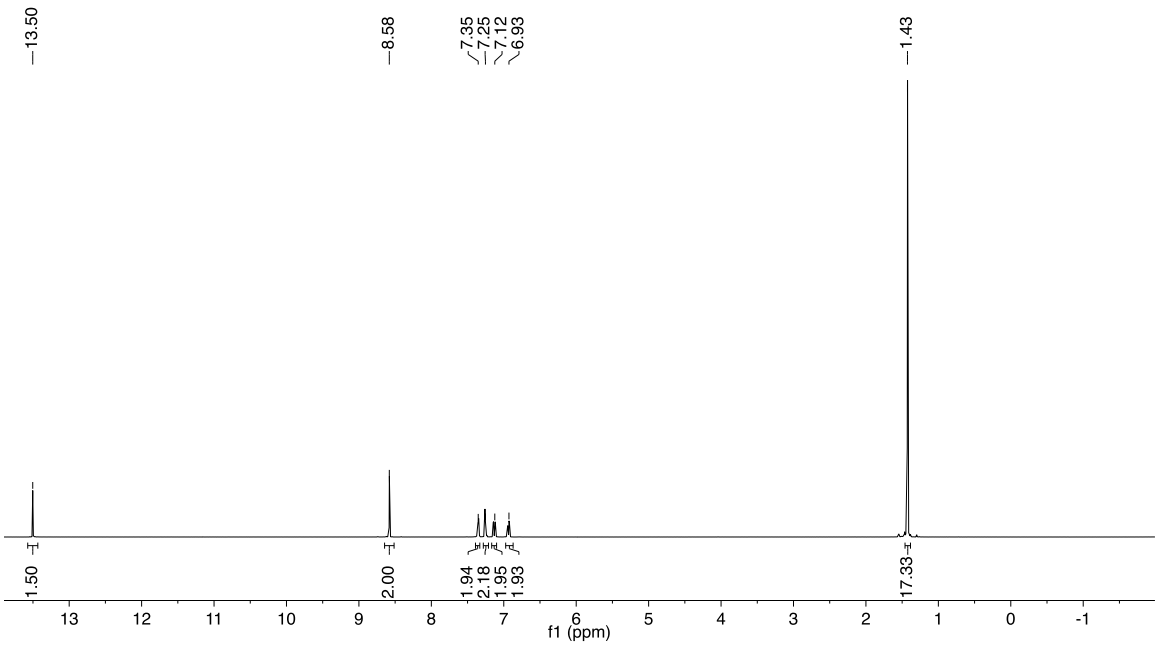
***N,N'*-Bis(3-*tert*-butylsalicylidene)-1,2-diaminobenzene [(salph-H)H_2]**

^{13}C NMR (126 MHz, $CDCl_3$)



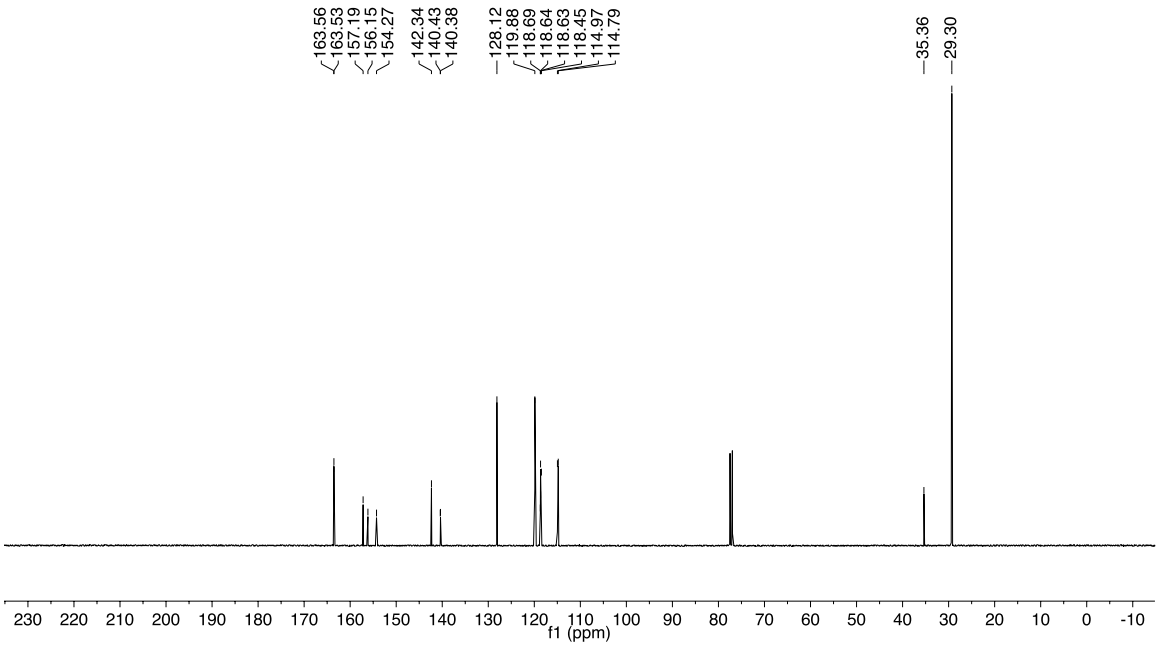
***N,N'*-Bis(3-*tert*-butyl-5-fluorosalicylidene)-1,2-diaminobenzene [(salph-F)H_2]**

^{1}H NMR (500 MHz, $CDCl_3$)



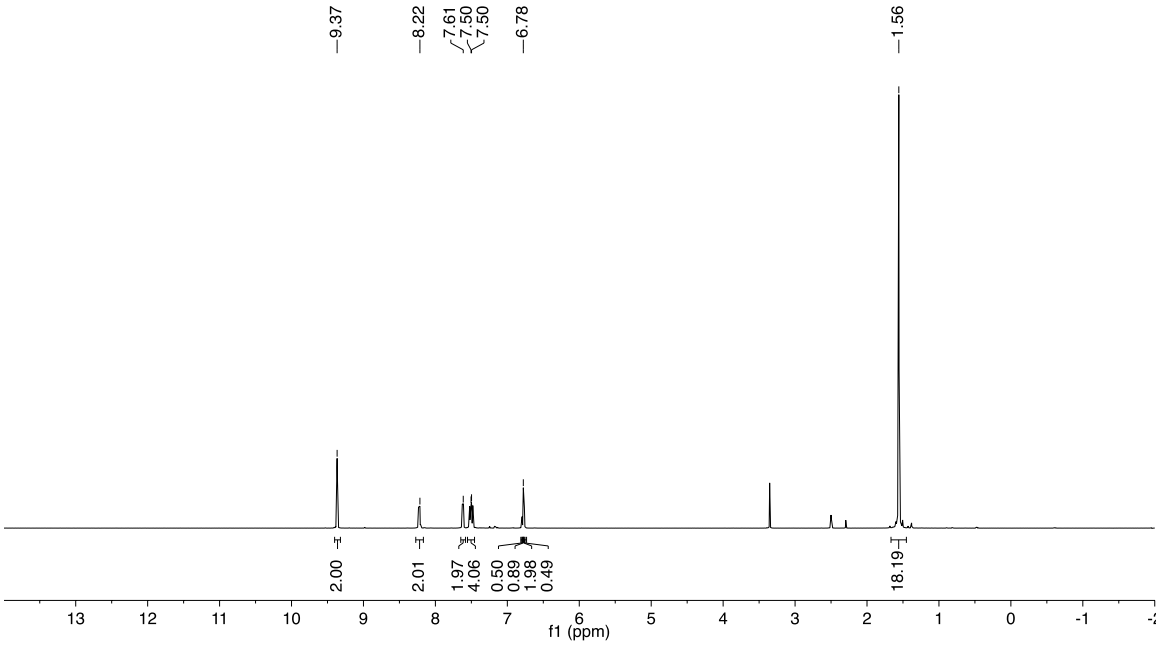
***N,N'*-Bis(3-*tert*-butyl-5-fluorosalicylidene)-1,2-diaminobenzene [(salph-F)H_2]**

^{13}C NMR (126 MHz, $CDCl_3$)



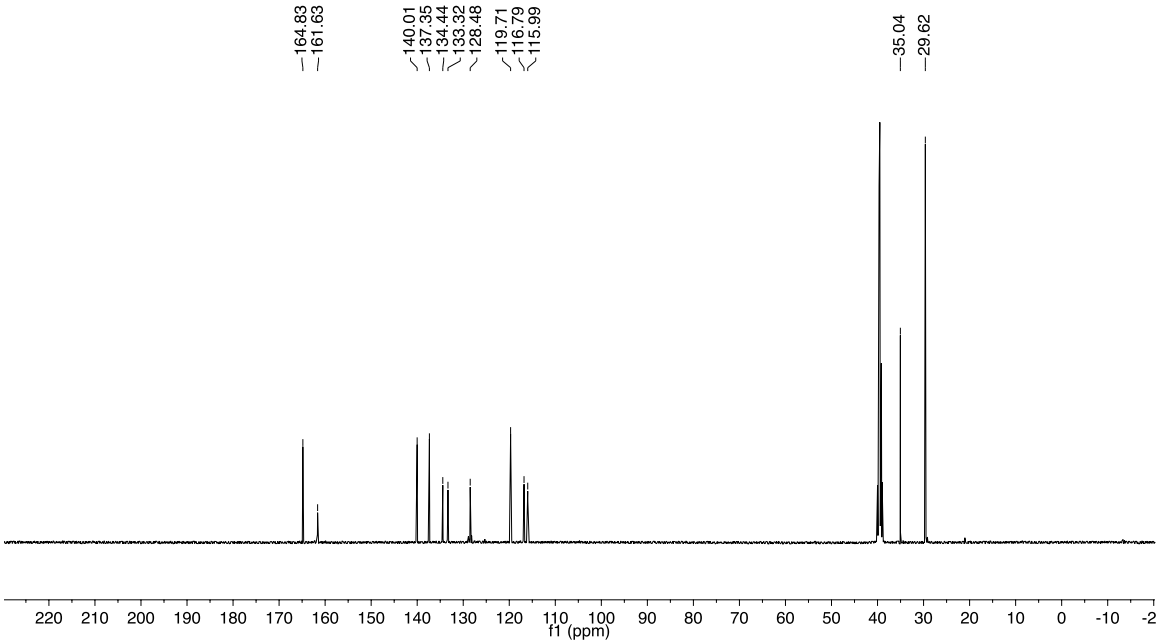
(salph-H)AlCl (2b)

^{1}H NMR (500 MHz, DMSO-d_6)



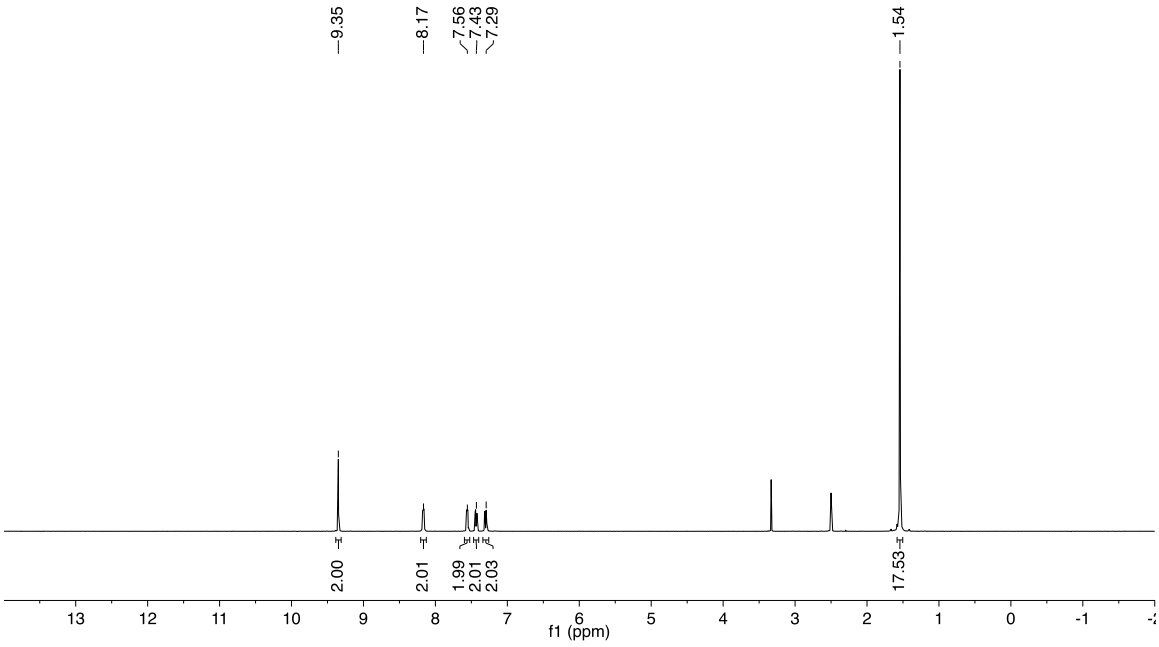
(salph-H)AlCl (2b)

^{13}C NMR (126 MHz, DMSO-d_6)



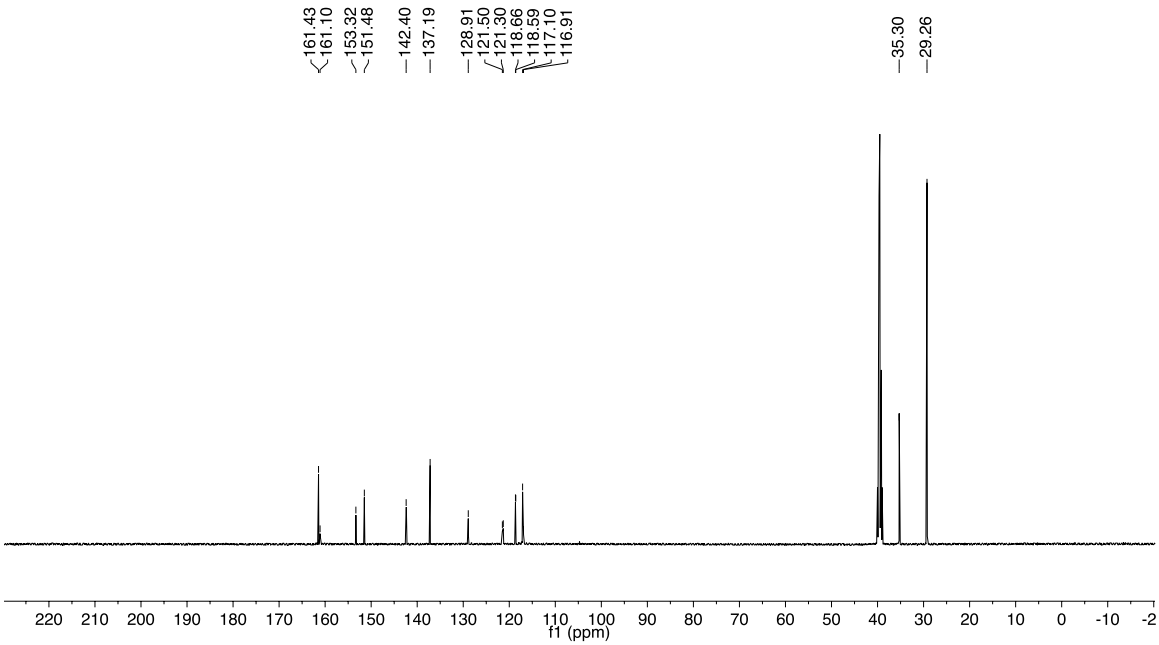
(salph-F)AlCl (2c)

^{1}H NMR (500 MHz, DMSO-d_6)



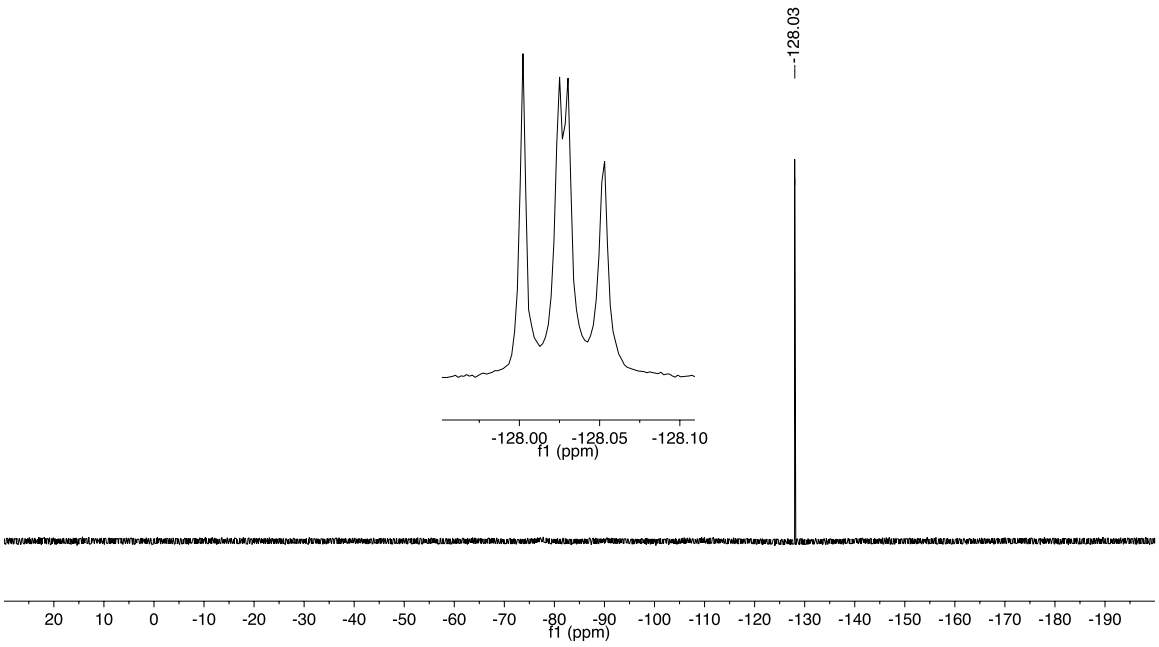
(salph-F)AlCl (2c)

^{13}C NMR (126 MHz, DMSO-d_6)



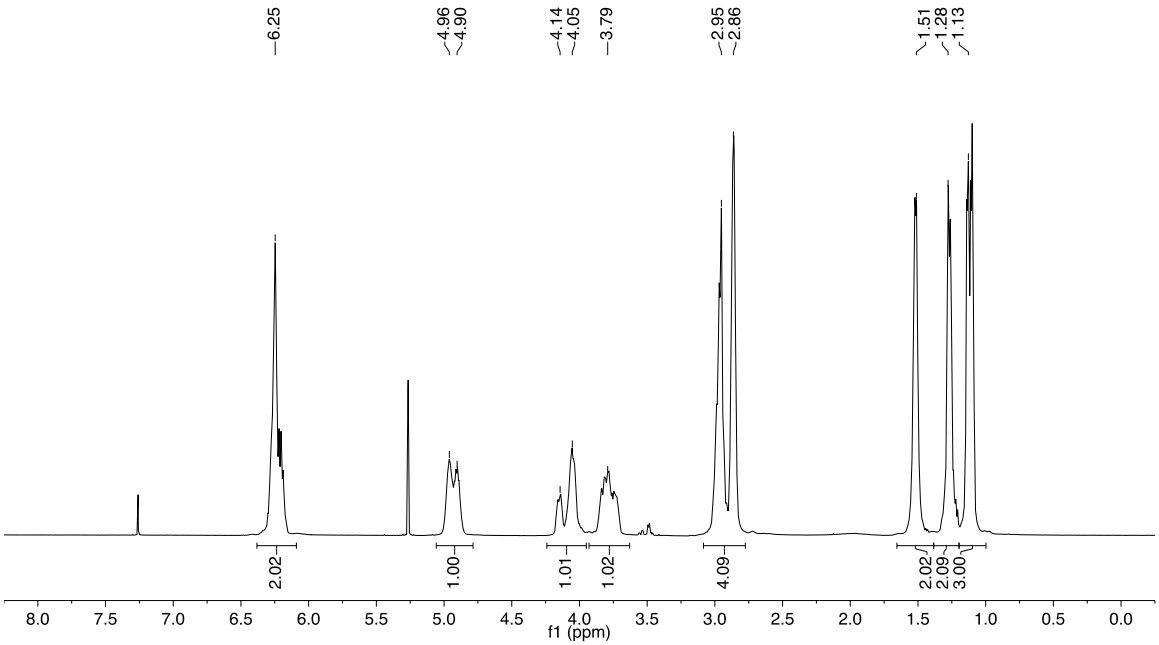
(salph-F)AlCl (2c)

^{19}F NMR (376 MHz, DMSO-d_6)



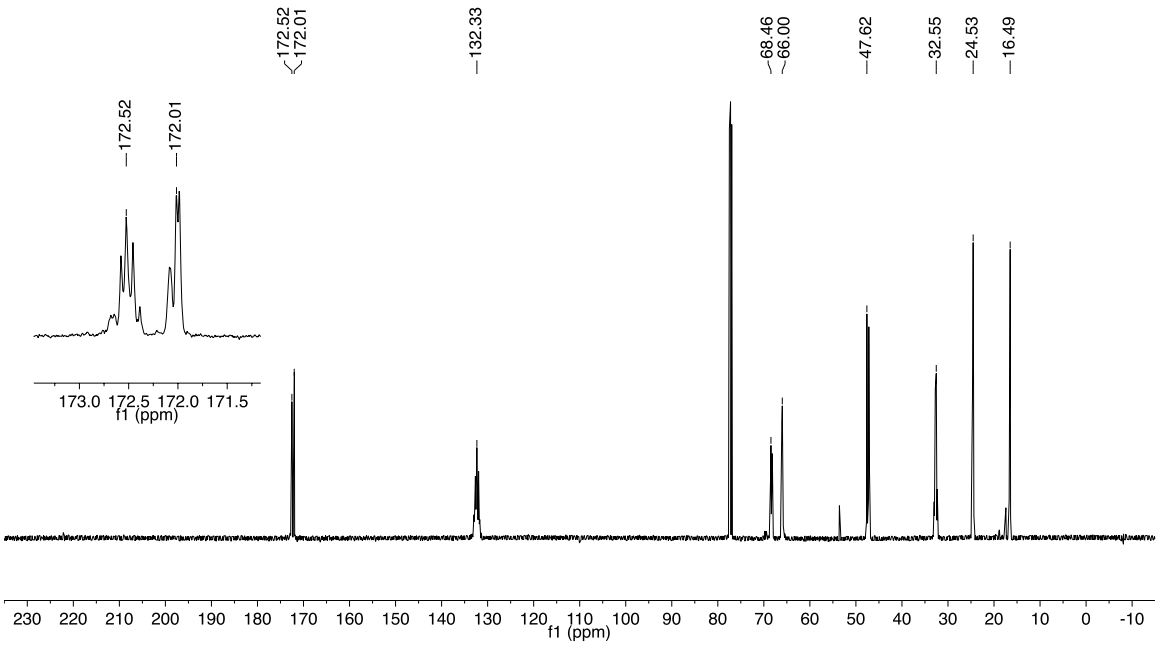
poly(1b-*alt*-PO) (Table 1, entry 2, t_{rxn} = 35 min)

^{1}H NMR (500 MHz, $CDCl_3$)



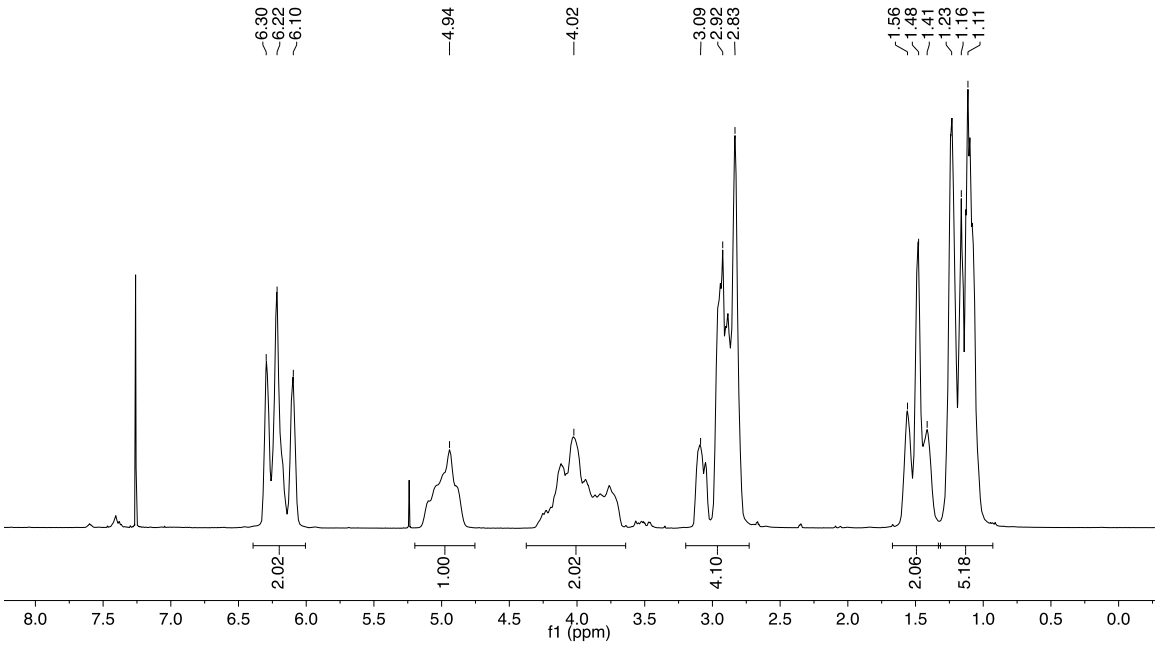
poly(1b-*alt*-PO) (Table 1, entry 2, t_{rxn} = 35 min)

^{13}C NMR (126 MHz, $CDCl_3$)



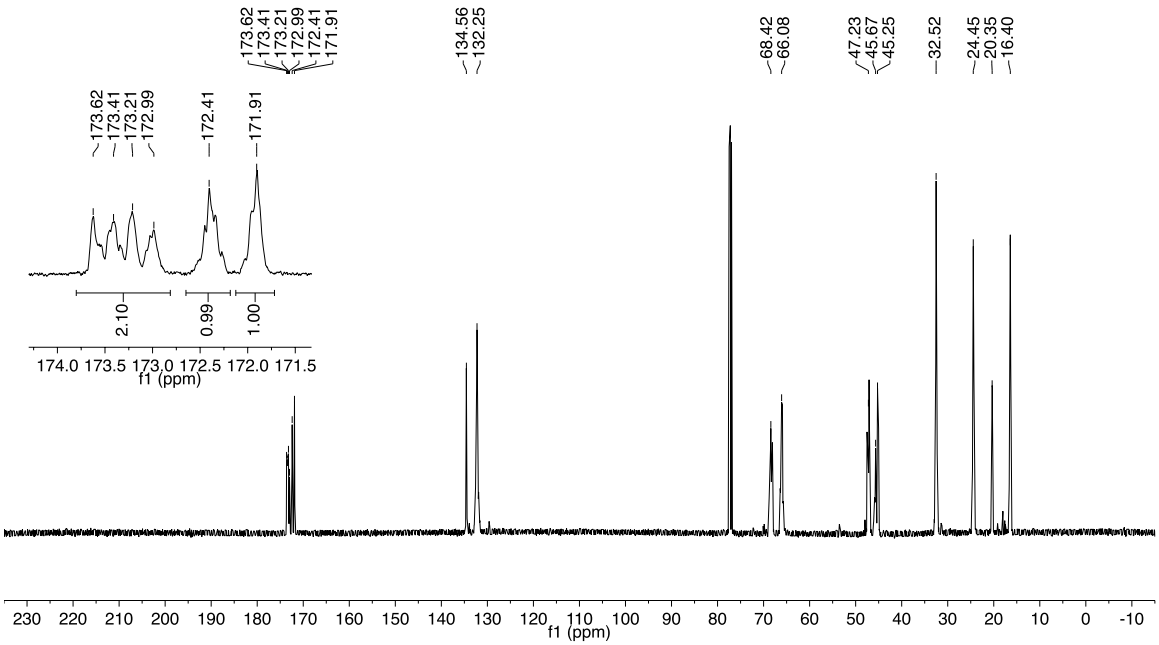
poly(1b-*alt*-PO) (Table 1, entry 2, t_{rxn} = 150 min)

^{1}H NMR (500 MHz, $CDCl_3$)



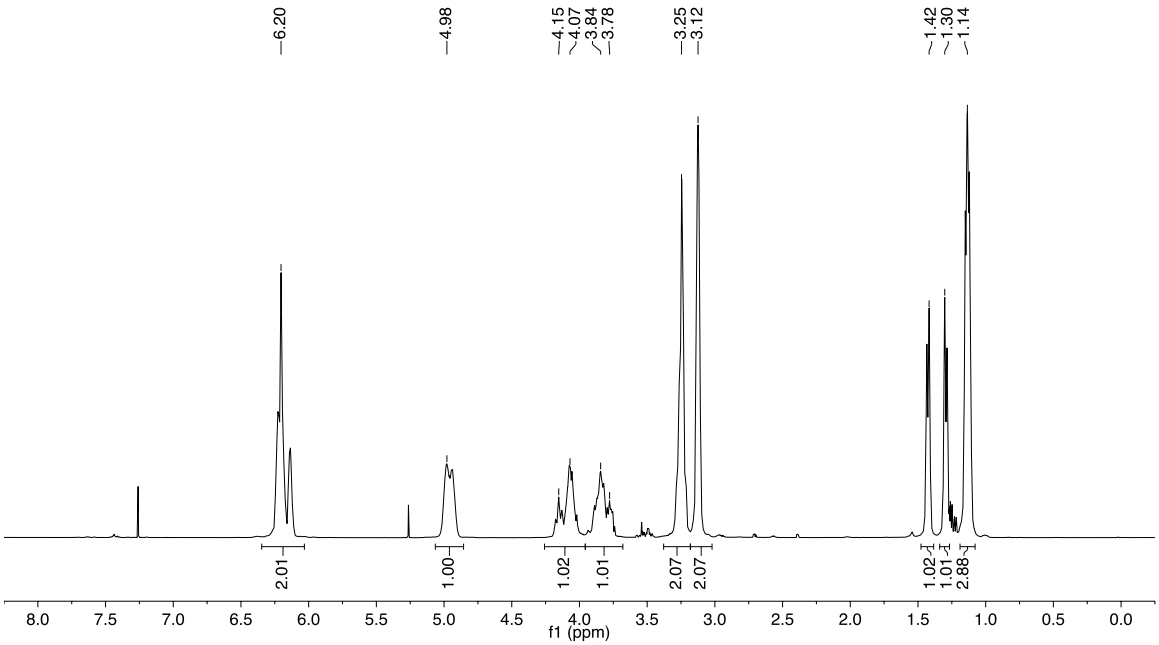
poly(1b-*alt*-PO) (Table 1, entry 2, t_{rxn} = 150 min)

^{13}C NMR (126 MHz, $CDCl_3$)



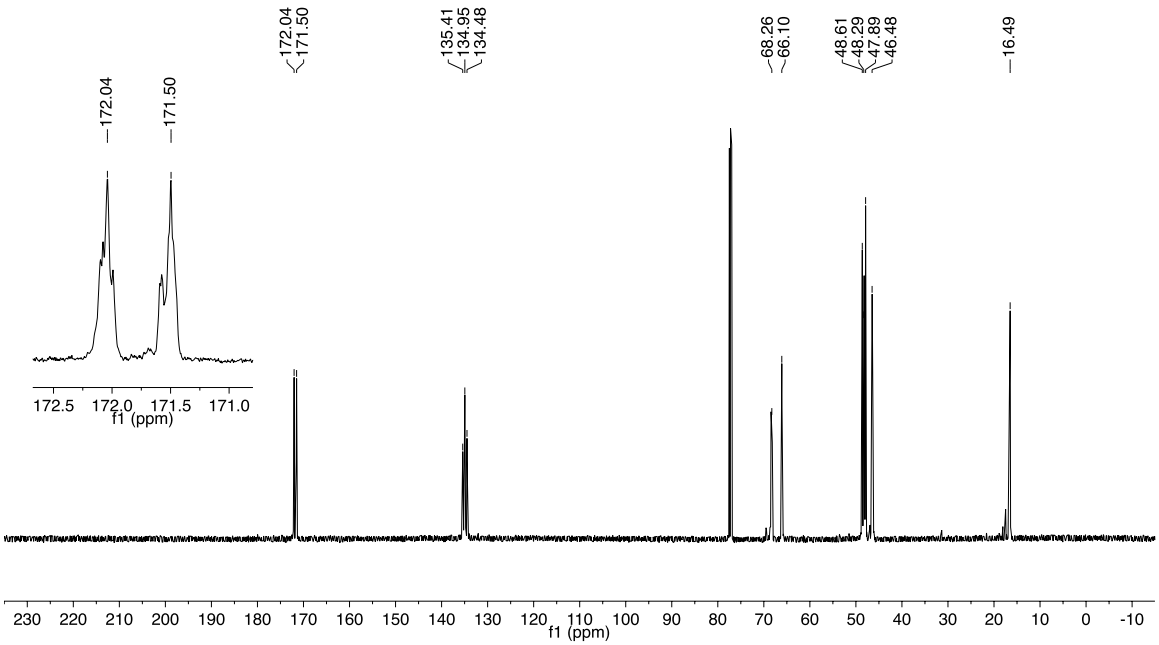
poly(1c-*alt*-PO) (Table 1, entry 3, t_{rxn} = 40 min)

^{1}H NMR (500 MHz, $CDCl_3$)



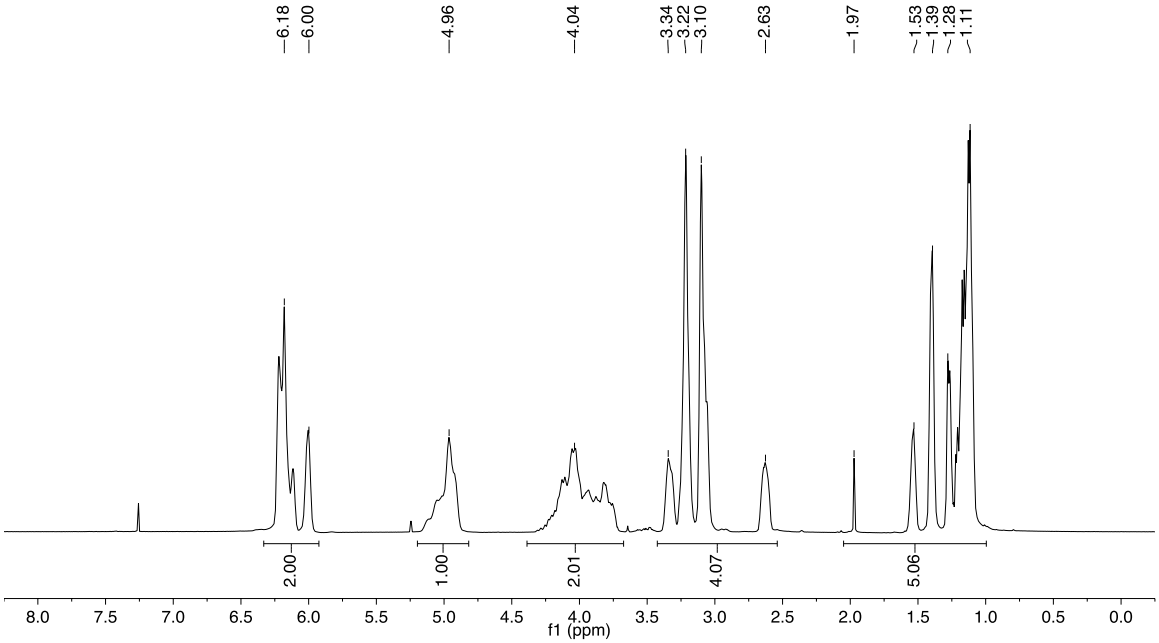
poly(1c-*alt*-PO) (Table 1, entry 3, t_{rxn} = 40 min)

^{13}C NMR (126 MHz, $CDCl_3$)



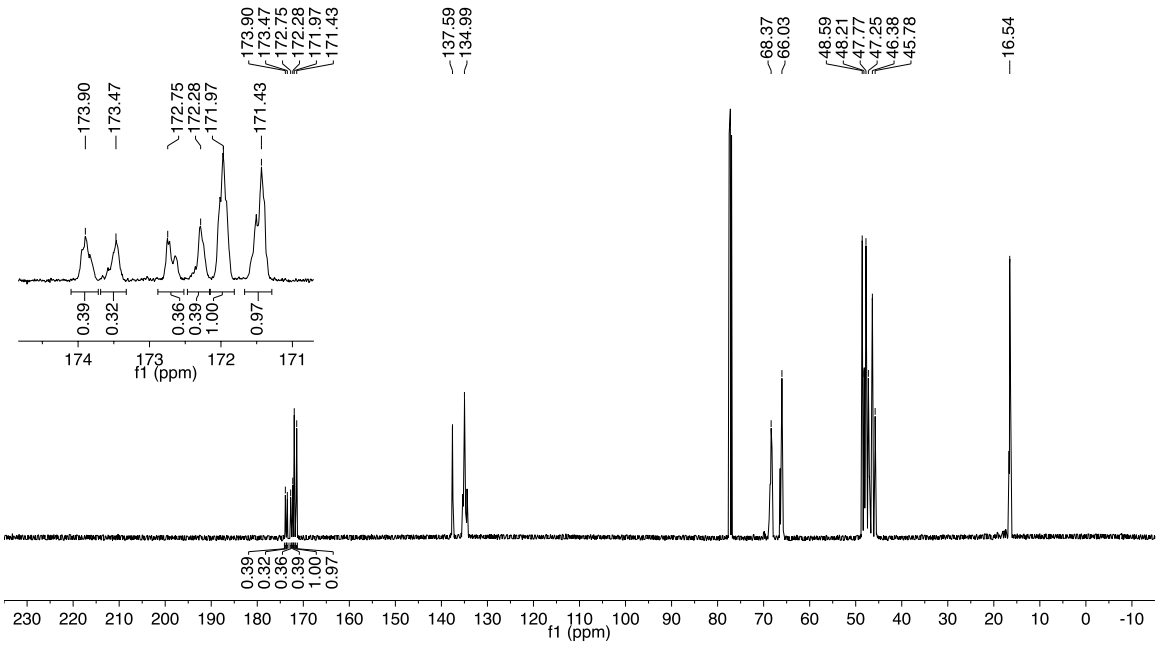
poly(1c-*alt*-PO) (Table 1, entry 3, t_{rxn} = 150 min)

^{1}H NMR (500 MHz, $CDCl_3$)



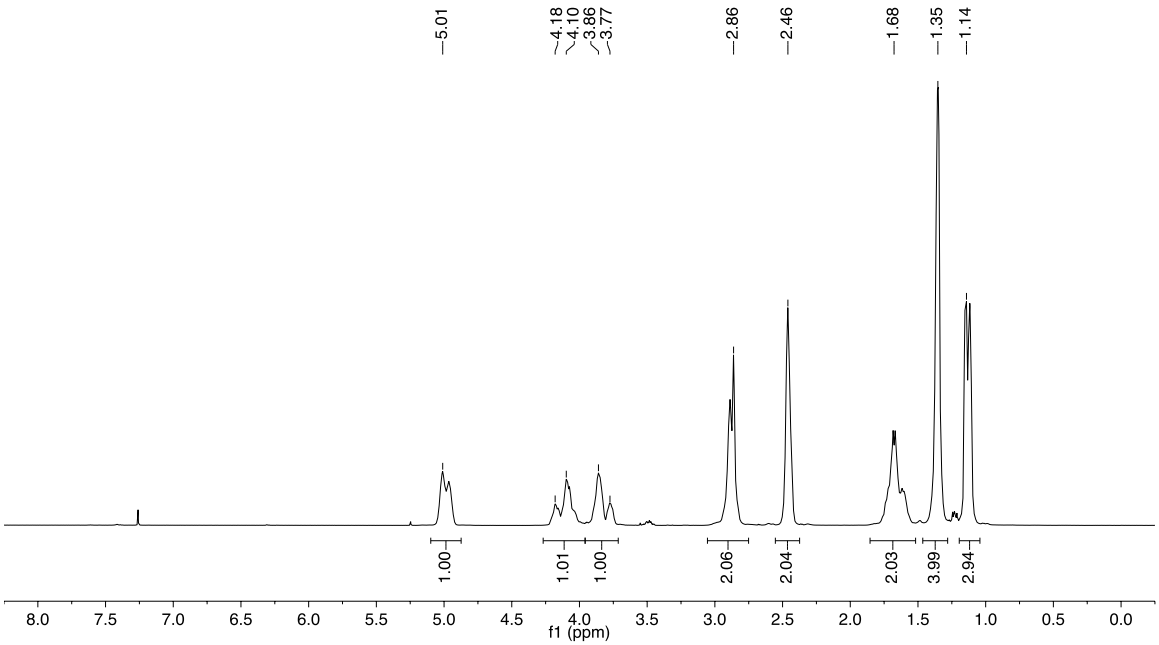
poly(1c-*alt*-PO) (Table 1, entry 3, t_{rxn} = 150 min)

^{13}C NMR (126 MHz, $CDCl_3$)



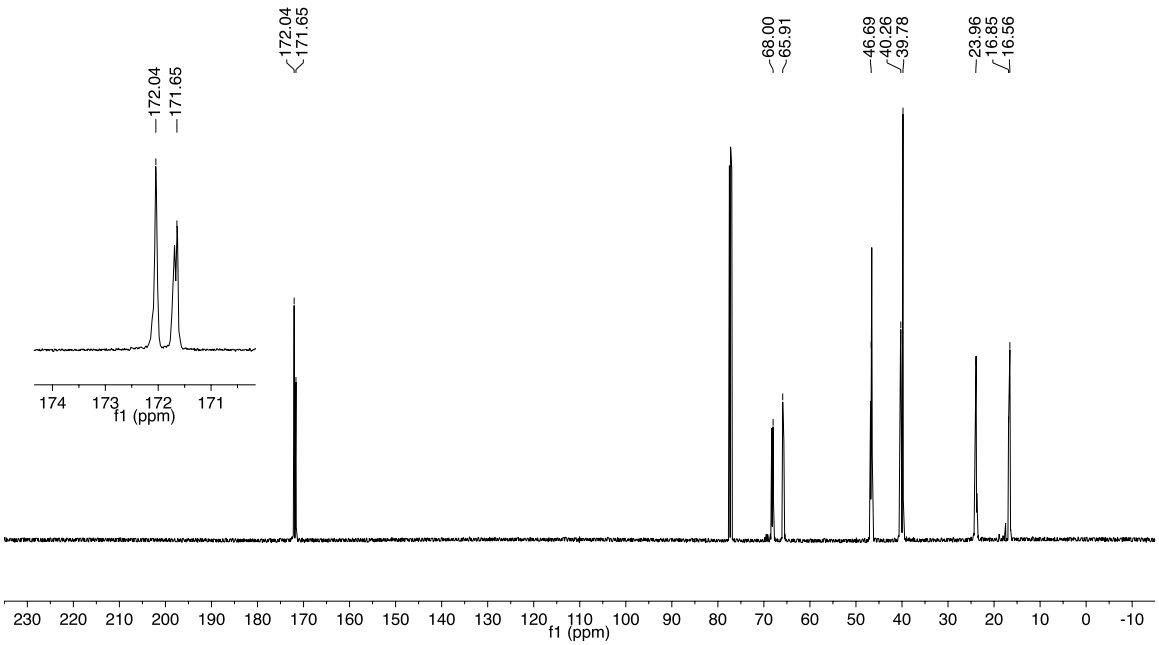
poly(1d-*alt*-PO) (Table 1, entry 4, t_{rxn} = 30 min)

^{1}H NMR (500 MHz, $CDCl_3$)



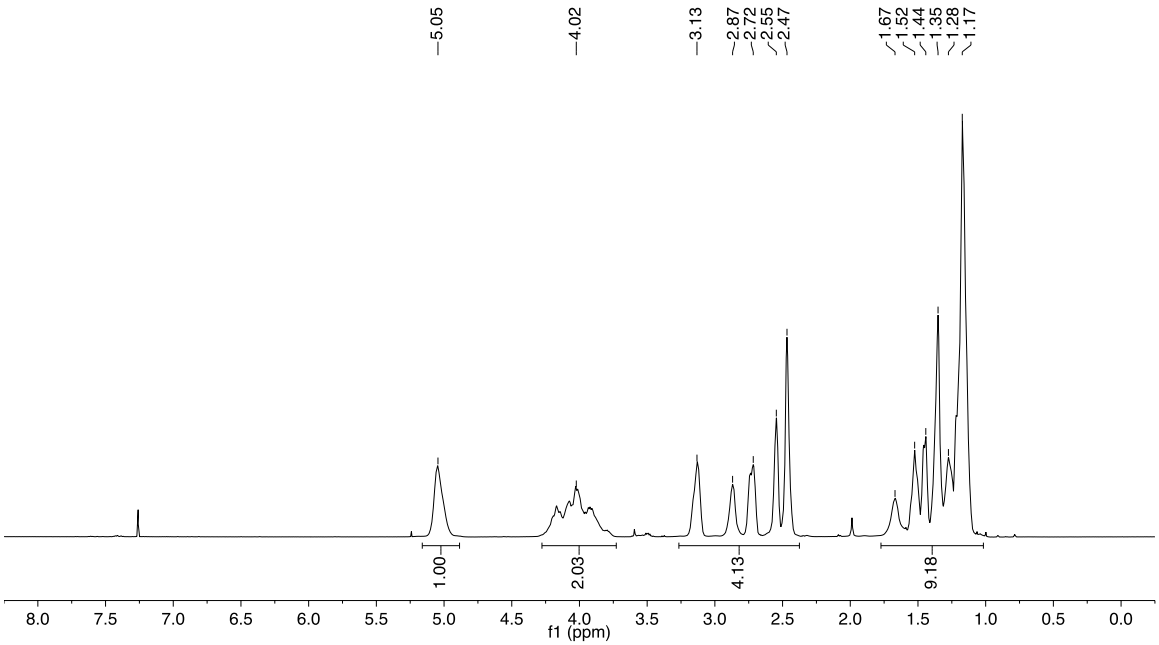
poly(1d-*alt*-PO) (Table 1, entry 4, t_{rxn} = 30 min)

^{13}C NMR (126 MHz, $CDCl_3$)



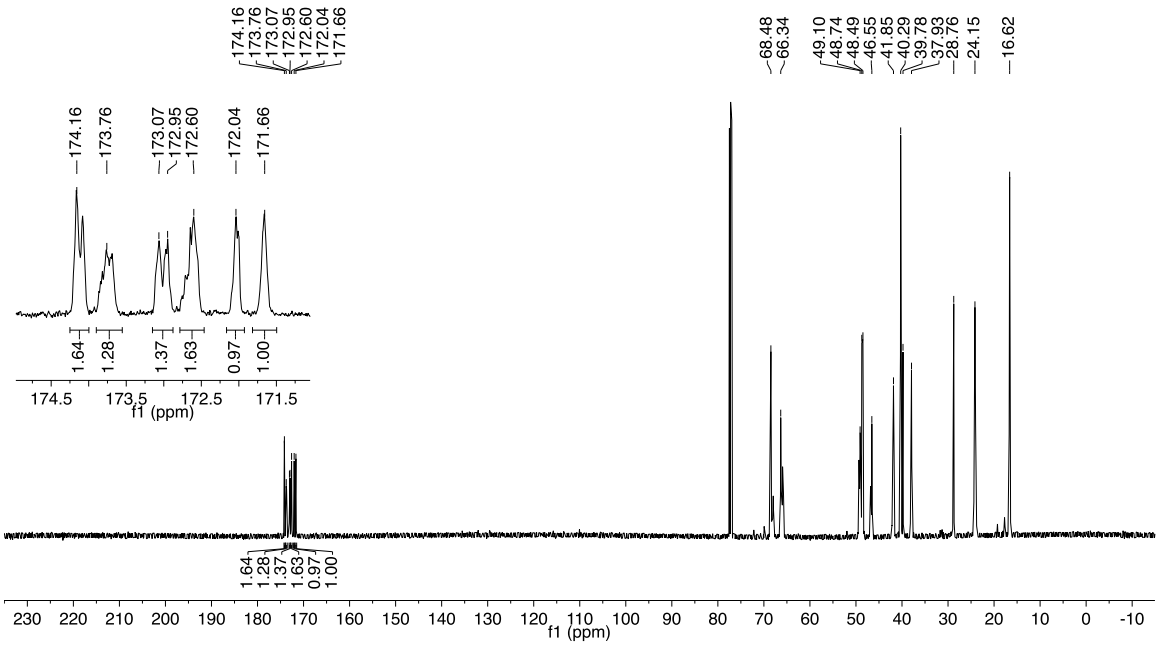
poly(1d-*alt*-PO) (Table 1, entry 4, t_{rxn} = 150 min)

^{1}H NMR (500 MHz, $CDCl_3$)



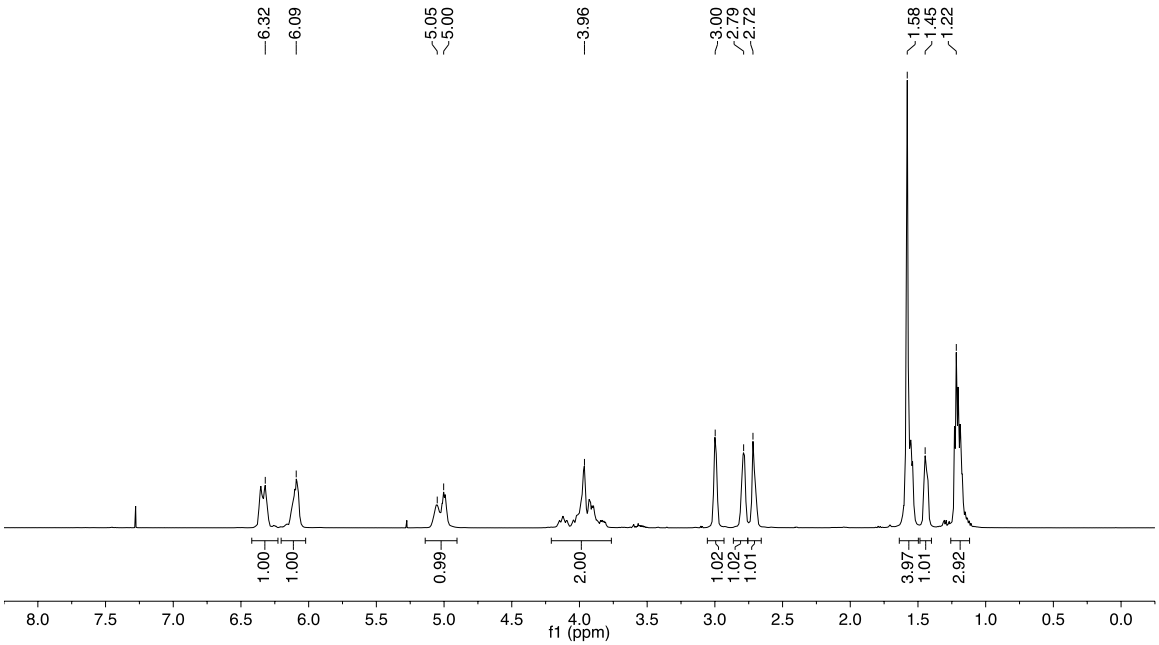
poly(1d-*alt*-PO) (Table 1, entry 4, t_{rxn} = 150 min)

^{13}C NMR (126 MHz, $CDCl_3$)



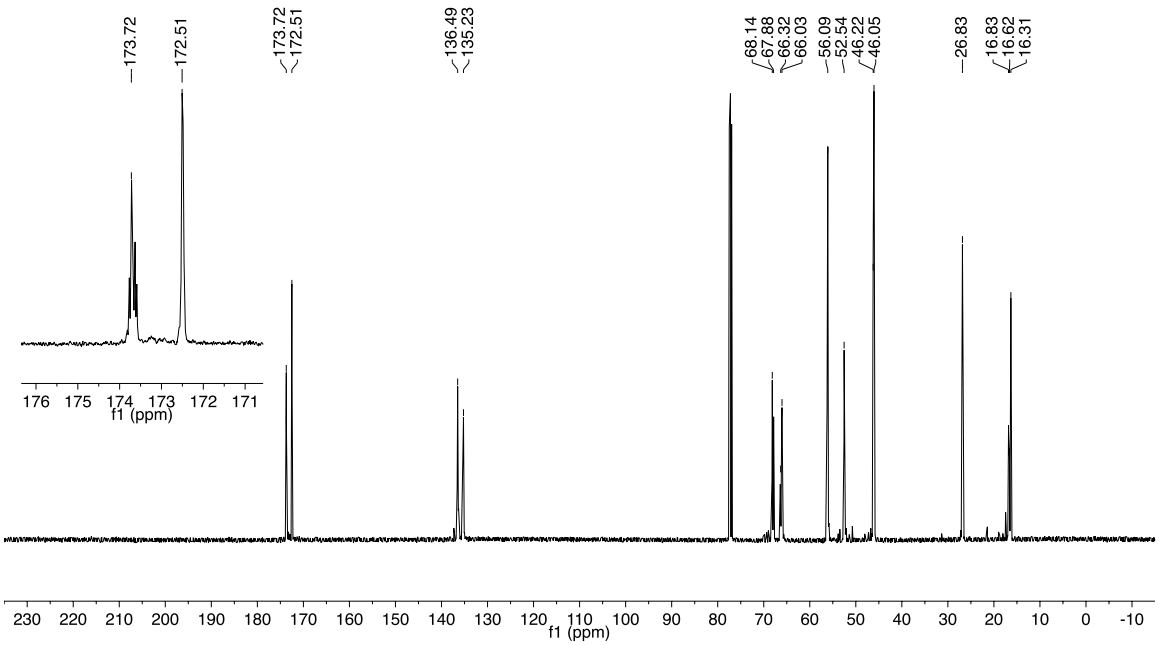
poly(1e-*alt*-PO) (Table 1, entry 5, t_{rxn} = 26 min)

^{1}H NMR (500 MHz, $CDCl_3$)



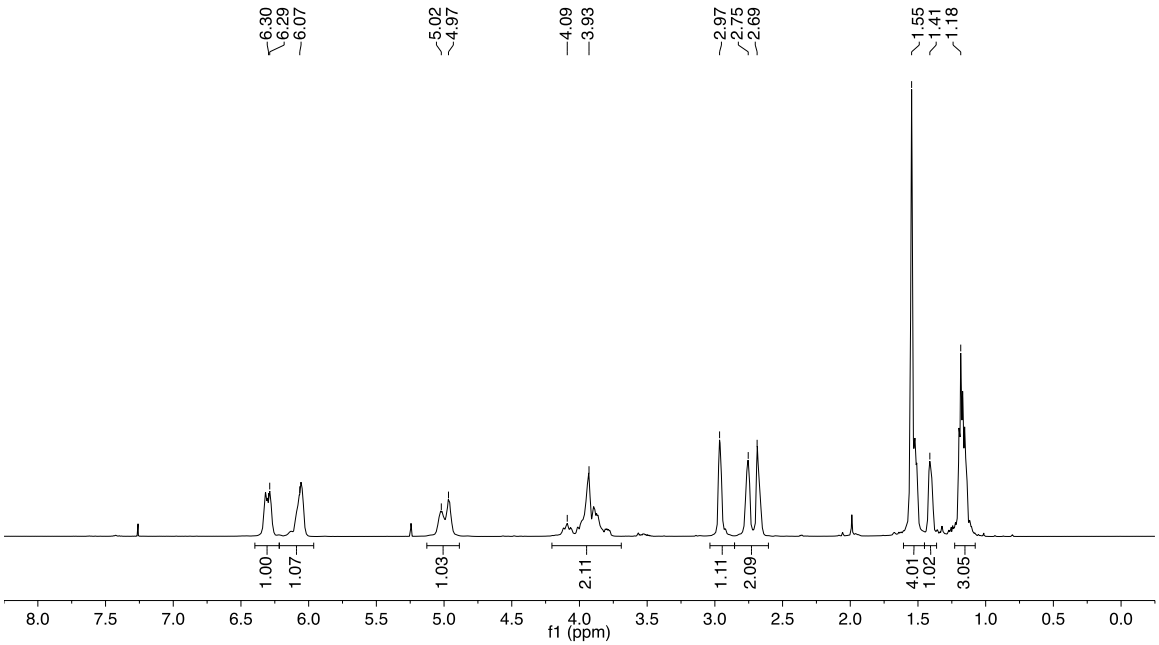
poly(1e-*alt*-PO) (Table 1, entry 5, t_{rxn} = 26 min)

^{13}C NMR (126 MHz, $CDCl_3$)



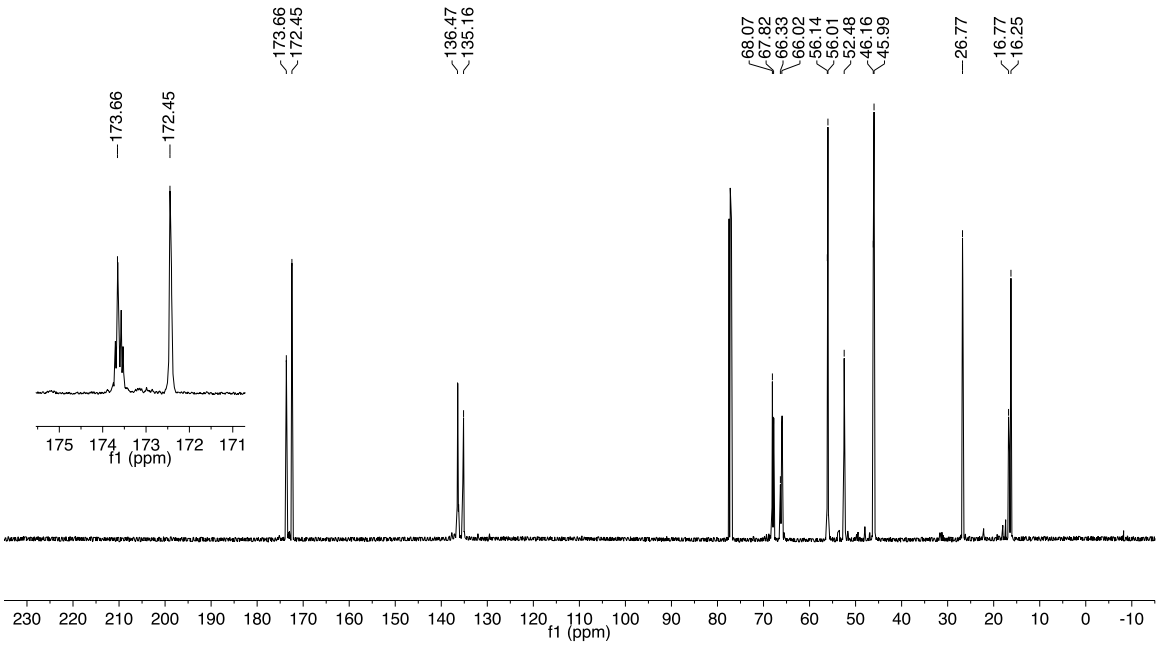
poly(1e-*alt*-PO) (Table 1, entry 5, t_{rxn} = 150 min)

^{1}H NMR (500 MHz, $CDCl_3$)



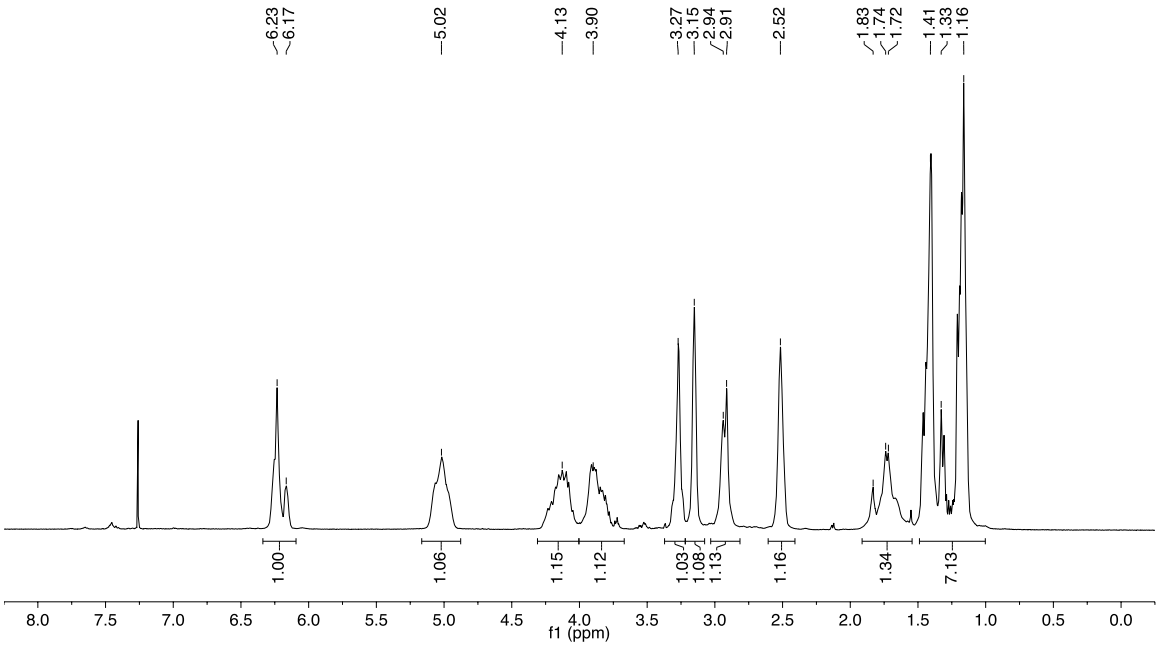
poly(1e-*alt*-PO) (Table 1, entry 5, t_{rxn} = 150 min)

^{13}C NMR (126 MHz, $CDCl_3$)



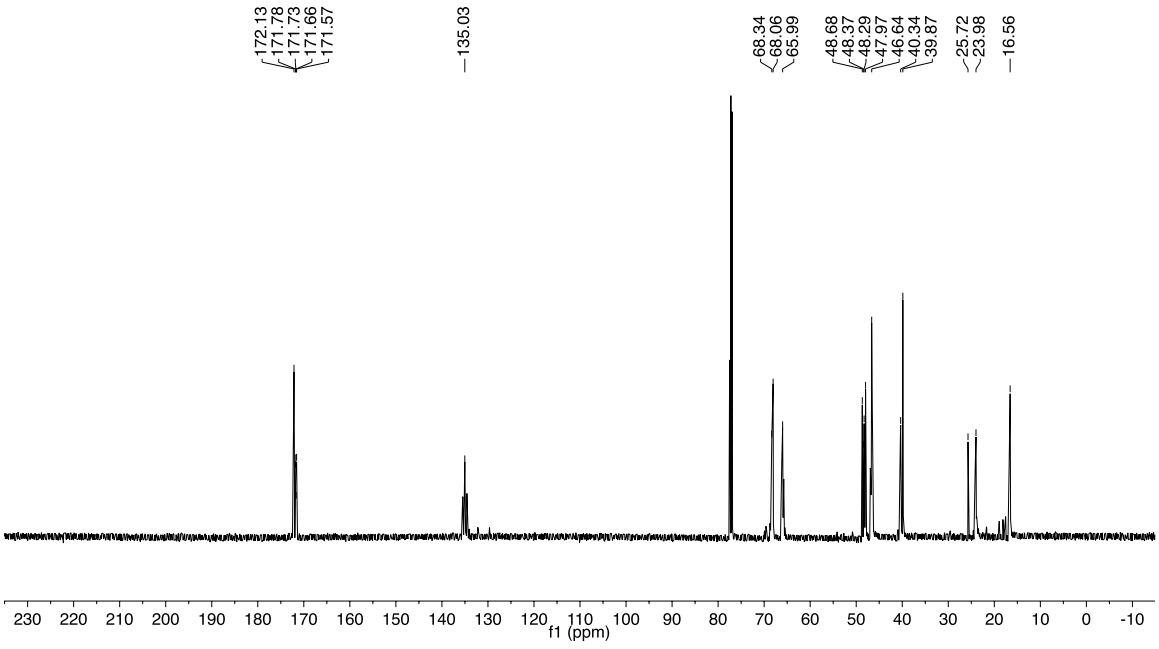
poly[(1c-*alt*-PO)-*b*-(1d-*alt*-PO)]

^{1}H NMR (500 MHz, $CDCl_3$)



poly[(1c-*alt*-PO)-*b*-(1d-*alt*-PO)]

^{13}C NMR (126 MHz, $CDCl_3$)



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